THE DEHYDROHALOGENATION OF HALO-ALKENYLAMINES WITH SODIUM AMIDE IN LIQUID AMMONIA

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By

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PREFACE

The presentation of this dissertation material is purposely given in detailed form to facilitate duplication by future investigators. The procedure followed in the synthesis of various members of a homologous series is given separately for each compound, even though it is basically the same for all members of the series.

In conformity with present usage in research reports, all temperatures refer to the centigrade scale; its symbol is omitted.

The boiling points are corrected values, and unless otherwise indicated, they represent boiling points at atmospheric pressure. The thermometers used in obtaining these boiling points were calibrated against a set of thermometers standardized by the Bureau of Standards.

Pressure readings below 10 mm. were obtained from a McLeod gauge; those above 10 mm. were obtained from a Zimmerli gauge calibrated at 4 mm. against the McLeod gauge.

All fractionations were carried out through a 90 cm. column packed with one-eighth inch Berl saddles.

The atomic refractions used throughout this research in calculating theoretical values of molar refractions were obtained from Karrer, Organic Chemistry, Second English Edition, Elsevier Publishing Co., Inc., 1946, p. 914.

The manner of listing references is the customary one for technical works. Journal abbreviations are the official ones of "Chemical Abstracts."

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CHAPTER I

INTRODUCTION AND REVIEW OF THE LITERATURE

The research described in this dissertation was conducted under the sponsorship of the Office of Naval Research, which specified in general that the compounds prepared should be liquids containing one or more amine groups and one or more unsaturated linkages, either ethylenic or acetylenic. They also specified that the compounds should contain no other functional groups. It was decided that the particular phase of the project represented by this dissertation should be confined to the synthesis of acetylenic amines. Although some compounds were prepared which deviated from this general type, they were prepared by the same method which led to the acetylenic amines in other cases, and they form an integral part of this phase of the research.

The field of acetylenic amines is a relatively new one, and references to it in the literature are few. The earliest reference to the synthesis of acetylenic amines which was located in the literature described in 1933 the work of Mannich and Chang, who prepared 1-phenyl-3-dialkylamino-propyne-1 compounds by the reaction of phenylacetylene, formaldehyde, and the appropriate secondary amine.[1] Jones Marszak, and Bader later reacted 1-hexyne, formaldehyde, and diethylamine to form 1-diethylamino-heptyne-2 in a similar manner.[2] Several patents have been granted covering the reaction of acetylene, formaldehyde, and amines to form the acetylenic amine, with only slight variations in the method.[3,4,5,6,7]

Jones, Lacey, and Smith prepared various amines containing both double and triple bonds by the reaction of alkenynyl halides with ammonia and amines.[8] Their paper also describes a study of the rearrangements encountered in these reactions. Johnson reacted 1,4-dichlorobutyne-2 with ammonia and amines to form the corresponding acetylenic diamines.[9]

In each of the above cases, the acetylenic amine was formed by the reaction of ammonia or an amine with a compound which already contained the triple bond. The reaction of acetylene with formaldehyde and an amine to form an acetylenic amine is hampered by the requirements of conducting the reaction under pressure and in the presence of a catalyst. The reaction of other alkynes with formaldehyde and ammonia or amines is limited to the higher members of the series, because of the high volatility of the lower alkynes. The reaction of an alkynyl halide with ammonia or an amine is limited by the difficulty of preparation of the appropriate alkynyl halide. All the methods previously used have been rather unsuitable for routine laboratory synthesis, and it was desirable to find a method whereby the acetylenic amines could be conveniently prepared using only equipment which would normally be found in an organic laboratory.

In order to avoid the difficulty of preparing alkynes or alkynyl halides, it was decided to form a halo-alkenylamine which could then be dehydrohalogenated to the corresponding acetylenic amine. These halo-alkenylamines were easily prepared by the reaction of 2,3-dibromopropene with amines. Although these halo-alkenylamines have not been previously reported in the literature, the reaction of a halogen compound with an amine is so well-known that a review of the literature on this subject is unnecessary.

It would be impractical to repeat here the entire history of the process of dehydrohalogenation for the purpose of introducing a triple bond. An excellent survey of previous research on the synthesis of acetylenes, including the process of dehydrohalogenation, has been published recently,[10] and only a brief summary will be presented here.

Alcoholic potassium hydroxide has been used most frequently for the synthesis of acetylenes by dehydrohalogenation. Potassium hydroxide has also been widely used in solid or molten form. Sodium amide, sodium hydroxide, sodium ethoxide, sodium anilide, sodium ethylmercaptide, potassium benzylate, potassium carbonate, potassium *tert*-butoxide, methylamine, diethylamine, pyridine, quinoline, soda lime, and the alkaline earth carbonates and hydroxides have also been used, although to a lesser extent. In the research described in this dissertation, only sodium amide was used for the dehydrohalogenation to produce a triple bond. For a more complete description of the use of other reagents, the reader is referred to the previously mentioned survey.[10]

Meunier and Desparmet, who prepared acetylene by reacting ethylene bromide with powdered sodium amide, were the first to use this reagent to produce a triple bond.[11] In a later publication, they described the preparation of some higher alkynes.[12] Bourguel has published several papers describing the preparation of alkynes by dehydrohalogenation with sodium amide in an inert solvent such as toluene, xylene, or various high-boiling petroleum fractions.[13,14,15,16] Since Bourguel's work, many investigators have reported the use of sodium amide as an agent for the introduction of a triple bond, usually in high-boiling, inert hydrocarbons as the solvent. The first use of liquid ammonia as a solvent for the dehydrohalogenation reactions to produce a triple bond was reported by Vaughn, Vogt, and Nieuwland.[17] The use of this solvent has since been reported by Ryden, Glavis, and Marvel[18] and by Campbell and O'Connor.[19] Liquid ammonia was used almost exclusively in the research described in this dissertation, since its use resulted in better yields and in greater ease of purification of the products.

To prepare the higher homologs of the various series, the coupling of alkyl halides with the sodium acetylide of acetylenic amines was used extensively in this research. The alkylation of sodium acetylide in liquid ammonia by alkyl halides was first reported by Lebeau and Picon.[20,21] They employed the alkyl iodides, but the bromides usually have been found to give higher yields. In place of the alkyl halides, the use of alkyl sulfates[22,23] and esters of p-toluenesulfonic acid[24] has been reported. These couplings are limited to the introduction of primary alkyl groups. Other halogen compounds react in a different manner to give various products.[21,25,26,27,28,29,30,31] For a more complete summary of previous research on these coupling reactions, the reader is again referred to the published survey of the synthesis of acetylenes.[10]

The second phase of the research described in this dissertation deals with the synthesis of N-substituted 2-propenylidenimines. While saturated aldehydes react with primary amines to form substituted imines of this same type, acrolein does not undergo this reaction. The normal reaction between a saturated aldehyde and a primary amine forms an aldimine, or Schiff base, by removal of water between the aldehyde and the amine. This reaction has long been known in the aromatic series. It has more recently been extended to the aliphatic series as described by Kahovec,[32] Tiollais,[33,34] Campbell, Sommers and Campbell,[35] Lilly & Co.,[36] and others. The synthesis of branched chain, aliphatic secondary imines has been reported by Clark and Wilson.[37] Kropp reported the reaction of alpha-substituted cinnamaldehydes with primary aromatic amines to yield Schiff bases[38] and the reaction of alpha-beta-substituted acroleins with primary aromatic amines to yield oils presumed to be Schiff bases.[39] Tiollais, in one of the papers referred to above,[34] reported the synthesis of the imines formed by reaction of crotonaldehyde with n-propylamine and with isopropylamine. No reference to the synthesis of simple imines by the reaction of unsubstituted acrolein with primary amines have been located in the literature. Carnahan and Hurd have reported that the reaction of acrolein with aniline yielded a resin,[40] and Mann reported that this reaction yielded a compound with the empirical formula $C_{18}H_{20}ON_2$.[41] Other reported reactions of acrolein with primary amino compounds have yielded products other than the imine.[42,43]

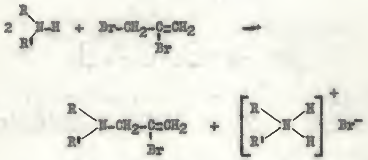
When an effort was made to synthesize secondary, acetylenic amines by the same method described in this dissertation for the synthesis of tertiary, acetylenic amines, it was found that an imine was formed. In each case, it was the imine which would have resulted from the formation of a Schiff base between acrolein and a primary amine, although acrolein itself does not undergo this reaction under normal conditions. Several attempts were made to synthesize these compounds by the reaction of acrolein with primary aliphatic amines, employing the conditions used by other investigators for preparing similar compounds, but all attempts resulted in the formation of resins.

This synthesis of these imines is very unusual, and offers a considerable insight into the mechanism of dehydrohalogenation reactions employing sodium amide. This mechanism will be discussed in Chapter VII of this dissertation.

CHAPTER II

PREPARATION OF INTERMEDIATES

The intermediate halo-alkenylamines used in this research have all been prepared by the reaction of 2,3-dibromopropene with a primary or secondary amine. The reaction is shown below:



In the reaction as applied to this research, R represents an alkyl group and R' represents a hydrogen atom, the same alkyl group as represented by R, or the 2-bromo-2-propenyl radical.

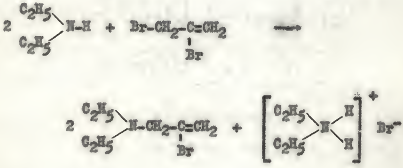
By observing the structure of 2,3-dibromopropene as shown above, it may be seen that the halogen atom attached to the central carbon is vinyl in nature and consequently is very inert. The other halogen atom is on a carbon atom once removed from the double bond, as in allyl bromide, and is extremely active. This great difference in the reactivity of the two halogen atoms insures that side reactions of the inert halogen atom with the amine will be held to a minimum and undoubtedly contributes greatly to the stability of the halo-alkenylamines formed.

These halo-alkenylamines have been successfully used in the crude form in the dehydrohalogenation reactions, but somewhat higher yields have been obtained when they were purified by distillation before use.

Since all these intermediates were found to be somewhat unstable, they were stored in dark bottles in a refrigerator where they remained for periods of several months with only slight decomposition.

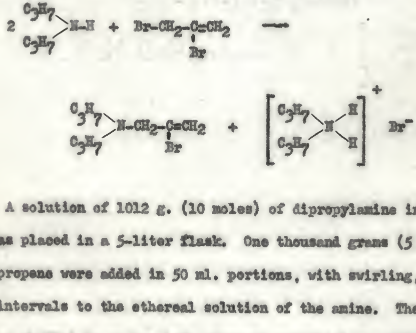
In every case, the amine hydrobromides which were formed in the reaction as shown above were preserved for recovery of the free amine, thereby avoiding considerable waste which might otherwise have occurred.

Synthesis of 1-Diethylamino-2-bromopropene-2



One thousand grams (5 moles) of 2,3-dibromopropene and a solution of 730 g. (10 moles) of diethylamine in 3 liters of ether were placed in the refrigerator in separate containers. When both were chilled to 10°, the 2,3-dibromopropene was added in 50 ml. portions at one-hour intervals, with swirling, to the ethereal solution of diethylamine, allowing the containers to remain in the refrigerator between additions. After the addition of the first portion of 2,3-dibromopropene, there was formed a white precipitate of diethylamine hydrobromide which became continuously heavier throughout the course of the additions. When the addition of 2,3-dibromopropene was complete, the reaction mass was removed from the refrigerator and allowed to come to room temperature by standing overnight. The diethylamine hydrobromide was then filtered off. The ether was removed from the filtrate by evaporation on a steam bath, some further precipitation occurring meanwhile. After the ether was removed, the residue was filtered again, and the filtrate was distilled through a Vigreux column under reduced pressure. The fraction boiling from 93-96° (corr.)/73 mm. [b.p. 54°/10 mm.] was collected. The yield was 820 g., which corresponded to 85% of the theoretical amount, based upon the 2,3-dibromopropene used.

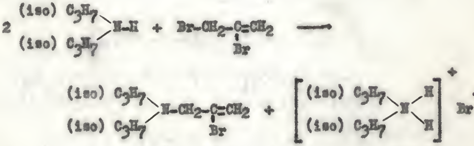
Synthesis of 1-Dipropylamino-2-bromopropene-2



$$2\,(C_3H_7)_2N\text{-}H + Br\text{-}CH_2\text{-}\underset{Br}{C}{=}CH_2 \longrightarrow (C_3H_7)_2N\text{-}CH_2\text{-}\underset{Br}{C}{=}CH_2 + \left[(C_3H_7)_2NH_2\right]^+ Br^-$$

A solution of 1012 g. (10 moles) of dipropylamine in 2 liters of ether was placed in a 5-liter flask. One thousand grams (5 moles) of 2,3-dibromopropene were added in 50 ml. portions, with swirling, at thirty-minute intervals to the ethereal solution of the amine. The reaction flask was chilled in an ice bath whenever necessary to prevent boiling of the solution. When the addition of 2,3-dibromopropene was complete, the reaction mass was allowed to stand at room temperature for twelve hours. The precipitated dipropylamine hydrobromide was filtered off. The filtrate was placed on a steam bath and the ether was slowly removed by evaporation, some further precipitation of dipropylamine hydrobromide occurring meanwhile. When the ether had been essentially removed, the solution was again filtered, and the filtrate was dried over solid sodium hydroxide. Fractionation of this material yielded 920 g. of 1-dipropylamino-2-bromopropene-2 boiling from 80-82° (corr.)/10 mm. This yield corresponded to 83% of the theoretical amount, based upon the 2,3-dibromopropene used.

Synthesis of 1-Diisopropylamino-2-bromopropene-2



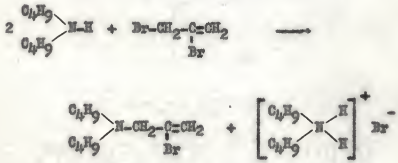
$$2\ \begin{matrix}(\text{iso})\ C_3H_7\\(\text{iso})\ C_3H_7\end{matrix}\!>\!N-H + Br-CH_2-\underset{Br}{C}=CH_2 \longrightarrow$$

$$\begin{matrix}(\text{iso})\ C_3H_7\\(\text{iso})\ C_3H_7\end{matrix}\!>\!N-CH_2-\underset{Br}{C}=CH_2 + \left[\begin{matrix}(\text{iso})\ C_3H_7\\(\text{iso})\ C_3H_7\end{matrix}\!>\!N\!<\!\begin{matrix}H\\H\end{matrix}\right]^{+} Br^{-}$$

[Due to the steric effect of the two isopropyl groups on the nitrogen atom, it was found necessary to impose considerably more strenuous conditions in carrying out this reaction.]

Twelve hundred and ten grams (10 moles) of diisopropylamine and 600 g. (3 moles) of 2,3-dibromopropene were mixed in a 3-liter, 3-necked, round-bottomed flask equipped with a stirrer, reflux condenser, and electric heating mantle. While stirring, gentle refluxing was maintained for a period of six hours. It was then necessary to discontinue stirring and heating and to filter the contents of the flask to remove the precipitated diisopropylamine hydrobromide. The precipitate was washed with a minimum amount of diisopropylamine, and the filtrate and washings were returned to the reaction flask. Stirring and refluxing were resumed and continued for an additional period of forty-eight hours. The contents of the flask were then filtered, and the filtrate was distilled. The excess of diisopropylamine was removed at atmospheric pressure until the temperature in the pot reached 125°. The distillation was then continued under reduced pressure, collecting the fraction boiling from 75-77.5° (corr.)/10 mm. This fraction weighed 468 g., corresponding to 71% of the theoretical amount, based upon the amount of 2,3-dibromopropene used.

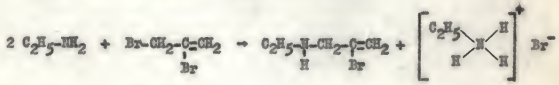
Synthesis of 1-Dibutylamino-2-bromopropene-2



$$2\,(C_4H_9)_2N\text{-}H + Br\text{-}CH_2\text{-}C(Br){=}CH_2 \longrightarrow (C_4H_9)_2N\text{-}CH_2\text{-}C(Br){=}CH_2 + \left[(C_4H_9)_2NH_2\right]^+ Br^-$$

One thousand and thirty-two grams (8 moles) of dibutylamine were dissolved in 2 liters of ether in a 5-liter flask. Eight hundred grams (4 moles) of 2,3-dibromopropene were added in 50 ml. portions, with swirling, over a period of three hours. The reaction mass was then allowed to stand at room temperature for twenty-four hours. The precipitated dibutylamine hydrobromide was filtered off and washed with ether, combining the washings with the original filtrate. The ether was removed from the filtrate by heating on a steam bath, and the residue was filtered again. This filtrate was distilled under reduced pressure, collecting the fraction boiling from 107-110° (corr.)/10 mm. [b.p. 80-82° (corr.)/2 mm.] . This fraction weighed 760 g., corresponding to 77% of the theoretical amount, based upon the 2,3-dibromopropene used.

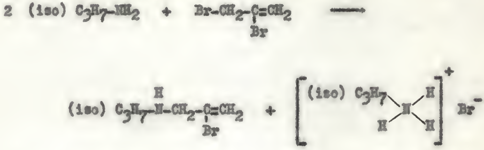
Synthesis of 1-Ethylamino-2-bromopropene-2



$$2\ C_2H_5\text{-}NH_2 + Br\text{-}CH_2\text{-}\underset{Br}{C}{=}CH_2 \rightarrow C_2H_5\text{-}\underset{H}{N}\text{-}CH_2\text{-}\underset{Br}{C}{=}CH_2 + \left[\overset{C_2H_5\qquad H}{\underset{H\qquad H}{N}}\right]^{+} Br^{-}$$

Nine hundred milliliters (about 10 moles) of commercial 70% ethylamine solution were placed in a 3-liter flask. Six hundred grams (3 moles) of 2,3-dibromopropene were added in 50 ml. portions, with swirling, over a period of two hours. The flask was chilled in an ice bath whenever necessary to prevent boiling of the solution. When the addition of 2,3-dibromopropene was complete, the mixture was boiled gently on a hot plate in the hood for twenty minutes. Solid sodium hydroxide was then cautiously added into the flask, shaking vigorously after each addition, until separation of the mixture into two layers occurred. The upper, organic layer was removed, dried over solid sodium hydroxide, and distilled rapidly through a Vigreux column, collecting the fraction boiling from 148-153°. This fraction weighed 350 g., corresponding to 71% of the theoretical amount, based upon the 2,3-dibromopropene used.

Synthesis of 1-Isopropylamino-2-bromopropene-2

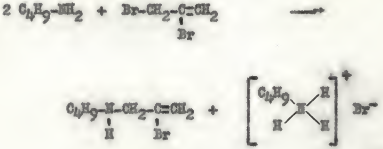


$$2\ (\text{iso})\ C_3H_7{-}NH_2 + Br{-}CH_2{-}\underset{Br}{C}{=}CH_2 \longrightarrow (\text{iso})\ C_3H_7{-}\overset{H}{N}{-}CH_2{-}\underset{Br}{C}{=}CH_2 + \left[(\text{iso})\ C_3H_7NH_3\right]^+ Br^-$$

A solution of 400 g. (6.8 moles) of isopropylamine in 1.5 liters of ether was placed in a 3-liter flask. Four hundred grams (2 moles) of 2,3-dibromopropene were added in 50 ml. portions, with swirling, over a period of three hours. The flask was chilled in an ice bath whenever necessary to prevent boiling of the solution. When the addition of 2,3-dibromopropene was complete, the flask was stoppered and allowed to stand at room temperature for forty-eight hours. The precipitated isopropylamine hydrobromide was then filtered off. The filtrate was heated on a steam bath until the ether was removed, dried over solid sodium hydroxide, and distilled under reduced pressure. The fraction boiling from 64-67°/27 mm. was collected. This fraction weighed 242 g., corresponding to 68% of the theoretical amount, based upon the amount of 2,3-dibromopropene used.

The compound may be purified by rapid distillation through a Vigreux column at atmospheric pressure, b.p. 158-160°, but this results in lower yields due to extensive decomposition in the pot.

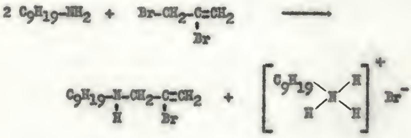
Synthesis of 1-n-Butylamino-2-bromopropene-2



$$2\ C_4H_9\text{-}NH_2 + Br\text{-}CH_2\text{-}\underset{Br}{C}{=}CH_2 \longrightarrow C_4H_9\text{-}\underset{H}{N}\text{-}CH_2\text{-}\underset{Br}{C}{=}CH_2 + \left[\begin{matrix} C_4H_9 & & H \\ & N & \\ H & & H \end{matrix}\right]^+ Br^-$$

Seven hundred and fifty grams (10.3 moles) of n-butylamine were dissolved in 2 liters of ether in a 5-liter flask. One thousand grams (5 moles) of 2,3-dibromopropene were added in 50 ml. portions, with swirling, over a period of three hours. The flask was cooled in an ice bath whenever necessary to prevent boiling of the solution. When the addition of 2,3-dibromopropene was complete, the mixture was allowed to stand at room temperature for twenty-four hours. The reaction mixture thus obtained was in two phases. About 1 liter of water was added into the flask, and the mixture was shaken vigorously to dissolve all the n-butylamine hydrobromide present. The layers were then separated, and the ether layer was dried over solid sodium hydroxide. The ether was removed by heating on a steam bath, and the residue was distilled under reduced pressure, collecting the portion boiling from 71-73° (corr.)/10 mm. The yield of 1-n-butylamino-2-bromopropene-2 was 715 g., corresponding to 74.5% of the theoretical amount, based upon the 2,3-dibromopropene used.

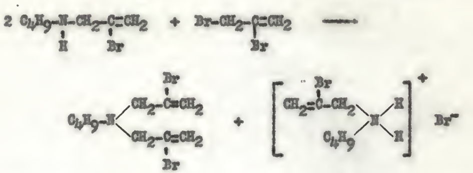
Synthesis of 1-Nonylamino-2-bromopropene-2



$$2\ C_9H_{19}\text{-}NH_2 + Br\text{-}CH_2\text{-}\underset{Br}{C}{=}CH_2 \longrightarrow C_9H_{19}\text{-}\underset{H}{N}\text{-}CH_2\text{-}\underset{Br}{C}{=}CH_2 + \left[C_9H_{19}NH_3\right]^+ Br^-$$

A solution of 450 g. (3.14 moles) of nonylamine in 750 ml. of ether was placed in a 3-liter flask and heated on a steam bath just to the boiling point. The flask was then removed from the steam bath, and 300 g. (1.5 moles) of 2,3-dibromopropene were added in small portions, with swirling, at such a rate that gentle boiling was just maintained. When the addition was complete, the solution was placed on a steam bath and the ether slowly removed by evaporation. When the ether was removed, the remaining solution was shaken vigorously with 500 ml. of saturated sodium hydroxide solution. The amine layer was removed, dried over solid sodium hydroxide, and distilled under reduced pressure. Distillation yielded, after the nonylamine fraction had been removed, 176 g. of 1-nonylamino-2-bromopropene-2, boiling from 91-93° (corr.)/1.4 mm. This yield corresponded to 45% of the theoretical amount, based upon the 2,3-dibromopropene used. A considerable amount of unidentified higher-boiling material remained in the pot.

Synthesis of N,N-bis-(2-Bromo-2-propenyl)-n-butylamine



Six hundred and seventy grams (3.5 moles) of 1-n-butylamino-2-bromopropene-2 and 250 ml. of toluene were mixed in a 3-liter, 3-necked, round-bottomed flask equipped with a stirrer, dropping funnel, and reflux condenser. The contents of the flask were heated to about 70° with an electric heating mantle, and heating was then discontinued. Over a period of one hour, 300 g. (1.5 moles) of 2,3-dibromopropene were added into the flask through the dropping funnel. On completion of this addition, heating was resumed; and the contents of the flask were maintained at about 100° for two hours. Into the flask were then added 500 ml. of saturated sodium hydroxide solution, stirring vigorously to insure complete decomposition of the amine hydrobromide which had formed. The amine layer was separated, dried over solid sodium hydroxide, and distilled under reduced pressure. A fraction consisting of 322 g. of 1-n-butylamino-2-bromopropene-2 was collected from 72-74°(corr.)/10 mm. The pressure was then reduced further, and the distillation was continued, collecting the distillate as rapidly as possible to minimize losses due to decomposition occurring in the pot. A fraction of 315 g. of N,N-bis-

(2-bromo-2-propenyl)-n-butylamine was collected from 95-99° (corr.)/1.3 mm. This yield corresponded to 67% of the theoretical amount, based upon the 2,3-dibromopropene used.

CHAPTER III

GENERAL PROCEDURES FOLLOWED IN CARRYING OUT REACTIONS IN LIQUID AMMONIA, INCLUDING THE PREPARATION OF SODIUM AMIDE

Although much research has been carried out in the past involving reactions in liquid ammonia, most frequently the procedures described required special equipment which is not normally found in an organic laboratory. The reactions described in this dissertation, on the other hand, have been carried out using equipment which usually is readily available. This chapter is included in the dissertation in order to present detailed information which should be helpful in making duplication of results less difficult.

The liquid ammonia used in these reactions was drawn from a cylinder into a 4-liter Dewar flask with a long, narrow neck. Liquid ammonia has been stored in this flask for days, when necessary, without undue loss, and the narrow neck facilitated pouring the ammonia.

The reactions were carried out in an ordinary 3-liter, 3-necked, round-bottomed Pyrex flask. A stirrer with glass or stainless steel blades was mounted through the center neck of the flask. It was necessary to use a very efficient stirrer, since the reaction mass became heavy at times due to precipitation of salts. A mercury-sealed stirrer was not used, since the reactions were carried out in the hood and since the loss of ammonia was unimportant. A second neck was used for additions, and in the third neck of the flask was mounted a reflux condenser. No water was passed through this condenser, and it served only as a safety tube. The reactions became very vigorous at times, and the contents of the flask sometimes boiled up into the condenser.

Most previous investigators who have used liquid ammonia as a solvent have reported the use of special equipment for condensing the escaping ammonia and returning it to the flask, often using dry ice and acetone reflux condensers of block tin. This also prevented the loss of reaction products which were otherwise carried off with the escaping ammonia. Although loss of product might occur in this manner in the preparation of the very volatile acetylenic hydrocarbons, the amines described in this dissertation were sufficiently high-boiling that this loss was proved negligible. A comparison of the cost of liquid ammonia with that of dry ice and of the relative amounts used revealed that there was very little difference in cost between replacing the ammonia which evaporated and condensing the ammonia with a dry ice and acetone reflux condenser and returning it to the flask.

Other investigators have also reported the strict maintenance of anhydrous conditions by attaching a soda-lime tube to the outlet from the flask and by using a gas-tight stirrer. In the reactions described in this dissertation, the ammonia was allowed to escape throughout the reaction, and this escaping ammonia prevented the entrance of harmful quantities of moisture into the flask.

The sodium amide used in these reactions was prepared in the reaction flask immediately prior to its use by the method of Vaughn, Vogt, and Nieuwland.[17] They showed that sodium amide prepared in this manner was considerably more soluble in liquid ammonia than the commercial product then available and was formed in a finely divided state which made it ideally suited for reaction. There has been placed on the market very recently a "free-flowing" sodium amide, advertised as a fine, white powder, which might be suitable for use, although it has not been used in these laboratories.

In general, it has been found advantageous to use a large excess of sodium amide in the dehydrohalogenations leading to the tertiary acetylenic amines, because of the formation of the sodium acetylides. Such an excess, however, definitely decreases the yields in the dehydrohalogenations leading to aldimines, and in the coupling reactions of alkyl halides with the sodium acetylides of acetylenic amines. The data supporting these statements are found in Table I.

TABLE I

EFFECT OF VARIOUS EXCESSES OF SODIUM AMIDE ON PERCENTAGE YIELDS IN SEVERAL REACTIONS IN LIQUID AMMONIA

Reaction	Compound Reacted with Sodium Amide	Moles of Sodium Amide per Mole of Other Reactant	Percentage Yield
1. Synthesis of 1-diethylaminopropyne-2	1-diethylamino-2-bromopropene-2	1.1 2.0 2.3	62 70 82.5
2. Synthesis of N-2-propenylidene-n-butylamine	1-n-butylamino-2-bromopropene-2	1.14 1.3 2.3	77 72 53
3. Synthesis of 1-diethylaminopentyne-2	1-diethylaminopropyne-2[a]	2.35 1.06	44 68

[a] Prior to addition of ethyl bromide.

For highest yields, it is suggested that a ratio of 2.3 moles of sodium amide be used for each mole of tertiary halo-alkenylamine in the dehydrohalogenation to produce the triple bond; that a ratio of 1.1 moles of sodium amide be used for each mole of secondary halo-alkenylamine in the dehydrohalogenation to produce the N-substituted 2-propenylidenimines; and that a ratio of 1.1 moles of sodium amide be used for each mole of dialkylamino-alkyne in producing sodium acetylides for coupling reactions. These proportions have not been followed throughout this project, since they were established as a result of this research. Many of the yields obtained could undoubtedly be improved by adoption of these ratios in the reactions.

In commencing a reaction, the reaction flask was half-filled with liquid ammonia. A powder funnel was used for the introduction of the ammonia since it was necessary that the funnel have a short, large-bore stem. Stirring was started and about one-half gram of crystalline ferric nitrate was added into the flask, imparting an orange color to the liquid ammonia when dissolved. The desired amount of metallic sodium was weighed under xylene, sliced into small, thin pieces, and replaced under xylene until addition into the ammonia. One or two small pieces of sodium were added into the flask and stirring was continued without further addition of sodium until the disappearance of the blue color. Vaughn, Vogt, and Nieuwland recommended the passing of dry air through the solution during this period, but this was dispensed with in these reactions. The air already in the flask apparently was sufficient to provide the oxygen necessary for the formation of the sodium oxide which, with the ferric salt, catalyzes the formation of sodium amide. The remaining sodium was then added, two or three pieces at a time, at intervals sufficient to prevent a too vigorous reaction. When the sodium was added too rapidly, there was considerable splattering within the flask which left a mirror of metallic sodium on the walls of the flask above the solution. When the addition of sodium was complete, stirring was continued for fifteen minutes after the last disappearance of the blue color. Liquid ammonia was then added into the flask to replace that which had evaporated and to bring up the total volume to about 2 liters. The solution was stirred unusually vigorously for a moment to wash down any metallic sodium adhering to the walls of the flask. The sodium amide in liquid ammonia was then ready for addition of the reactant.

A dropping funnel for this addition was mounted in that neck of the flask which had been used for the addition of the sodium. It was usually found necessary to add halogen compounds into the reaction mass very slowly, while the acetylenic amines could be added rather rapidly.

Throughout the earlier stages of the reaction, the total volume was maintained between one and one-half and two liters, adding liquid ammonia whenever necessary. The rate of evaporation of liquid ammonia was relatively high during the preparation of the sodium amide and during the initial reaction period, but it was quite low during the later portion of the reaction period. Since it was desirable to have a minimum volume of liquid ammonia remaining in the flask at the end of the reaction period, further additions of ammonia were discontinued at such a time that there would be remaining a total volume of about 750 ml. at the end of the reaction period. It was usually found that if the total volume were brought up to two liters five hours before the end of the reaction period and no further additions of ammonia made, the total volume would be about 750 ml. at the end of the reaction period.

During the reaction, observation of the contents of the flask was hindered by formation of a heavy coating of frost on the outside of the flask due to condensation of atmospheric moisture. This inconvenience was overcome by pouring a few drops of alcohol on the outside wall of the flask to form a small window for the purpose of observation.

When the reaction period was complete and the total volume had decreased to about 750 ml., 600 ml. of water and then 600 ml. of ether were added very cautiously into the flask with stirring. These were not added until the volume had decreased to the proper level, whether the reaction time was exceeded or not. When the ice had melted from the flask, its contents were filtered to remove the very small amount of iron which was present and to assist in breaking up the water-ether emulsion. The layers were separated, and the water layer was discarded. The ether layer was dried over solid sodium hydroxide, filtered, and heated on a steam bath to remove the ether. The residue from the ether layer was then fractionated, often under reduced pressure.

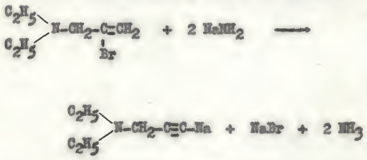
The acetylenic amines have been isolated from the ether layer by extraction with dilute hydrochloric acid. The acid solution was then made strongly basic by the addition of a large excess of saturated sodium hydroxide solution, causing the separation of an upper, water-insoluble layer. This layer was removed and dried over solid sodium hydroxide prior to distillation. This method of isolation is less satisfactory for the acetylenic amines than the one described above, however, from the standpoints of yields obtained and simplicity. Moreover, the use of this method is impossible for the isolation of the aldimines, due to the ease with which they are hydrolysed in acid solution.

If desired, the dehydrohalogenation of the halo-alkenylamines to produce the acetylenic amines and the coupling of the sodium acetylide of these amines with an alkyl halide may be carried out without isolation of the acetylenic amines. In this event, the alkyl halide is added into the flask after completion of the reaction period for the dehydrohalogenation, and stirring is continued for the proper period for the coupling reaction. This method is illustrated in the synthesis of 1-diethylaminoheptyne-2 described in Chapter IV.

CHAPTER IV

SYNTHESIS OF TERTIARY MONO-ACETYLENIC AMINES

Synthesis of 1-Diethylamino-propyne-2



$$\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!\!>N-CH_2-\underset{\displaystyle Br}{C}=CH_2 \;+\; 2\,NaNH_2 \;\longrightarrow$$

$$\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!\!>N-CH_2-C\equiv C-Na \;+\; NaBr \;+\; 2\,NH_3$$

Fifty-three grams (2.3 moles) of metallic sodium were converted into sodium amide in liquid ammonia, and the resulting sodium amide was reacted with 192 g. (1 mole) of 1-diethylamino-2-bromopropene-2 for a period of eight hours in liquid ammonia. The isolation was carried out as previously described.

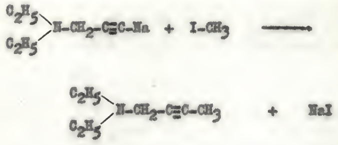
Fractionation yielded 91.5 g. of 1-diethylamino-propyne-2, boiling from 120-121°(corr.). This yield corresponded to 82.5% of the theoretical amount, based upon the 1-diethylamino-2-bromopropene-2 used.

The following physical constants and analytical data were determined for this compound:

B.p.	120-121° (corr.)
n_D^{25}	1.4296
D_4^{25}	0.8042
Mr_D	Theoretical, 36.46; found, 36.10
N, %	Theoretical, 12.60; found, 12.29

This compound has been previously reported in the literature,[6] but has not been prepared in this manner previously.

Synthesis of 1-Diethylamino-butyne-2



$$\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\rangle N\text{-}CH_2\text{-}C\equiv C\text{-}Na \;+\; I\text{-}CH_3 \longrightarrow$$

$$\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\rangle N\text{-}CH_2\text{-}C\equiv C\text{-}CH_3 \;+\; NaI$$

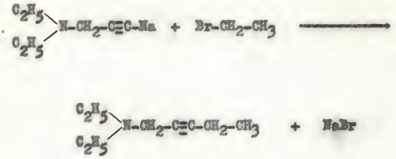
Twenty grams (0.87 mole) of metallic sodium were converted into sodium amide in liquid ammonia, and the resulting sodium amide was reacted in liquid ammonia for one hour with 89 g. (0.8 mole) of 1-diethylamino-propyne-2. One hundred and twenty-four grams (0.87 mole) of methyl iodide were then added into the flask, the addition requiring about two hours. Stirring was continued for a period of five hours after the completion of the addition. The isolation of the product was carried out as previously described.

Fractionation yielded 73 g. of 1-diethylamino-butyne-2, boiling from 152.5-153° (corr.). This corresponded to 73% of the theoretical amount, based upon the 1-diethylamino-propyne-2 used.

The following physical constants and analytical data were determined for this compound:

B.p.	152.5-153° (corr.)
n_D^{25}	1.4413
D_4^{25}	0.8075
Mr_D	Theoretical, 41.08; found, 40.97
N, %	Theoretical, 11.19; found, 11.19

Synthesis of 1-Diethylamino-pentyne-2



$$\begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix}\!\!>N\text{-}CH_2\text{-}C\equiv C\text{-}Na + Br\text{-}CH_2\text{-}CH_3 \longrightarrow \begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix}\!\!>N\text{-}CH_2\text{-}C\equiv C\text{-}CH_2\text{-}CH_3 + NaBr$$

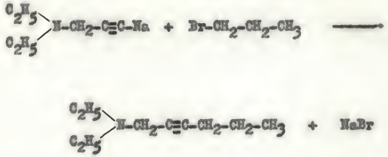
Thirty grams (1.3 moles) of metallic sodium were converted into sodium amide in liquid ammonia, and the resulting sodium amide was reacted for one hour in liquid ammonia with 111 g. (1 mole) of 1-diethylamino-propyne-2. One hundred and forty-two grams (1.3 moles) of ethyl bromide were added into the flask, and stirring was continued for a period of eight hours after the completion of the addition. The isolation of the product was carried out as previously described.

Fractionation yielded 82 g. of 1-diethylamino-pentyne-2, boiling from 168.4-169.9° (corr.). This yield corresponded to 59% of the theoretical amount, based upon the 1-diethylamino-propyne-2 used.

The following physical constants and analytical data were determined for this compound:

B.p.	168.4-169.9° (corr.)
n_D^{25}	1.4402
D_4^{25}	0.8029
Mr_D	Theoretical, 45.70; found, 45.72
N, %	Theoretical, 10.06; found, 10.11

Synthesis of 1-Diethylamino-hexyne-2



$$\begin{array}{l}C_2H_5\\C_2H_5\end{array}\!\!>N\text{-}CH_2\text{-}C\equiv C\text{-}Na \;+\; Br\text{-}CH_2\text{-}CH_2\text{-}CH_3 \longrightarrow \begin{array}{l}C_2H_5\\C_2H_5\end{array}\!\!>N\text{-}CH_2\text{-}C\equiv C\text{-}CH_2\text{-}CH_2\text{-}CH_3 \;+\; NaBr$$

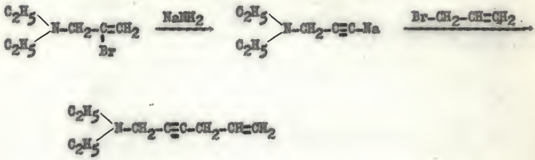
Twenty-five grams (1.09 moles) of metallic sodium were converted into sodium amide in liquid ammonia, and the resulting sodium amide was reacted in liquid ammonia for one hour with 85 g. (0.765 mole) of 1-diethylamino-propyne-2. Stirring was continued for a period of nine hours after the addition was complete. The isolation of the product was carried out as previously described.

Fractionation yielded 85 g. of 1-diethylamino-hexyne-2, boiling from 187.4-188.4° (corr.). This yield corresponded to 72.5% of the theoretical amount, based upon the 1-diethylamino-propyne-2 used.

The following physical constants and analytical data were determined for this compound:

B.p.	187.4-188.4° (corr.)
n_D^{25}	1.4431
D_4^{25}	0.8058
Mr_D	Theoretical, 50.33; found, 50.44
N, %	Theoretical, 9.14; found, 9.02

Synthesis of 1-Diethylamino-hex-5-en-2-yne



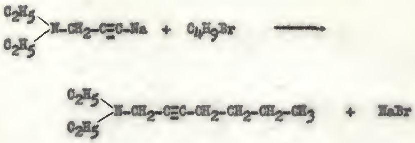
[It was found necessary to carry out this reaction in a solvent other than liquid ammonia, since the reaction did not proceed in liquid ammonia to yield the desired product. This bears out the work of other investigators who have found that the reaction of allyl halides with sodium acetylides in liquid ammonia yielded anomalous products.[28,30]]

One hundred and forty-four grams (6.25 moles) of metallic sodium were converted into sodium amide in liquid ammonia in a 3-liter, 3-necked, round-bottomed flask equipped with a stirrer, dropping funnel, and reflux condenser. When the conversion was complete, 1.5 liters of xylene were added into the flask as the ammonia evaporated. When the ice had melted from the flask, the contents were heated with an electric heating mantle until gentle refluxing began. Through the dropping funnel, 384 g. (2.0 moles) of 1-diethylamino-2-bromopropene-2 were added into the flask. Refluxing was continued for a period of five hours after completion of this addition. The contents of the flask were then cooled somewhat to permit the addition of allyl bromide. Five hundred grams (4.13 moles) of allyl bromide were then added into the flask at such a rate that gentle refluxing was maintained without external heating. After the addition, heating was resumed; and refluxing was continued for a period of two hours. The reaction mass was then poured over 2 kg. of cracked ice, and the entire mass was stirred vigorously. The upper, organic layer was removed and extracted twice with 500 ml. portions of dilute hydrochloric acid, each portion containing 2 moles of hydrogen chloride. These hydrochloric acid extracts were combined and made strongly basic by the addition of an excess of saturated sodium hydroxide solution, causing the separation of an upper, water-insoluble layer. This layer was removed, dried over solid sodium hydroxide, and fractionated under reduced pressure, collecting the fraction boiling from 52-53° (corr.)/11 mm. This fraction weighed 99 g., corresponding to 33% of the theoretical amount, based upon the 1-diethylamino-2-bromopropene-2 used.

The following physical constants and analytical data were determined for this compound:

B.p.	52-53° (corr.)/11 mm.
n_D^{25}	1.4452
D_4^{25}	0.8085
Mr_D	Theoretical, 49.85; found, 49.81
N, %	Theoretical, 9.26; found, 9.20

Synthesis of 1-Diethylamino-heptyne-2



$$\begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix}\!\!>N-CH_2-C\equiv C-Na + C_4H_9Br \longrightarrow \begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix}\!\!>N-CH_2-C\equiv C-CH_2-CH_2-CH_2-CH_3 + NaBr$$

(A) Synthesis from 1-diethylamino-propyne-2:

Seventeen and one-half grams (0.76 mole) of metallic sodium were converted into sodium amide in liquid ammonia, and the resulting sodium amide was reacted for one hour in liquid ammonia with 60 g. (0.54 mole) of 1-diethylamino-propyne-2. One hundred and four grams (0.76 mole) of n-butyl bromide were then added into the flask, and stirring was continued for a period of eight hours after the addition was complete. The isolation of the product was carried out as previously described.

Fractionation yielded 54 g. of 1-diethylamino-heptyne-2, boiling from 84-85° (corr.)/10 mm. This yield corresponded to 60% of the theoretical amount, based upon the 1-diethylamino-propyne-2 used.

(B) Synthesis from 1-diethylamino-2-bromopropene-2:

Twenty-eight grams (1.22 moles) of metallic sodium were converted into sodium amide in liquid ammonia, and the resulting sodium amide was reacted for six hours with 96 g. (0.5 mole) of 1-diethylamino-2-bromopropene-2. At the end of this reaction period, 98 g. (0.715 mole) of n-butyl bromide were added into the flask, and stirring was continued for a period of six hours after completion of this addition. The isolation of the product was carried out as described previously.

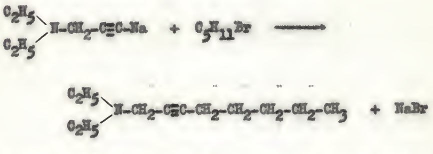
Fractionation yielded 46 g. of 1-diethylamino-heptyne-2, boiling from 84-85° (corr.)/10 mm. This yield corresponded to 55% of the theoretical amount, based upon the 1-diethylamino-2-bromopropene-2 used.

The following physical constants and analytical data were determined for this compound:

B.p.	84-85° (corr.)/10 mm.
n_D^{25}	1.4450
D_4^{25}	0.8071
Mr_D	Theoretical, 54.94; found, 55.16
N, %	Theoretical, 8.37; found, 8.31

This compound has been previously reported in the literature,[2] but has not been previously prepared in this manner.

Synthesis of 1-Diethylamino-octyne-2



$$(C_2H_5)_2N\text{-}CH_2\text{-}C{\equiv}C\text{-}Na + C_5H_{11}Br \longrightarrow (C_2H_5)_2N\text{-}CH_2\text{-}C{\equiv}C\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3 + NaBr$$

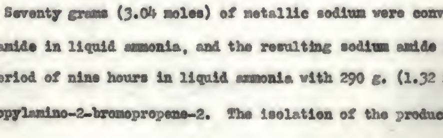
Twenty-three grams (1 mole) of metallic sodium were converted into sodium amide in liquid ammonia, and the resulting amide was reacted for one hour with 85 g. (0.765 mole) of 1-diethylamino-propyne-2 in liquid ammonia. One hundred and fifty-one grams (1 mole) of n-amyl bromide were then added into the flask, and stirring was continued for a period of ten hours after the completion of the addition. The isolation of the product was carried out as previously described.

Fractionation yielded 91 g. of 1-diethylamino-octyne-2, boiling at 100° (corr.)/10 mm. This yield corresponded to 66% of the theoretical amount, based upon the 1-diethylamino-propyne-2 used.

The following physical constants and analytical data were determined for this compound:

B.p.	100° (corr.)/10 mm.
n_D^{25}	1.4466
D_4^{25}	0.8097
Mr_D	Theoretical, 59.55; found, 59.78
N, %	Theoretical, 7.73; found, 7.69

Synthesis of 1-Diisopropylamino-propyne-2



$$\begin{matrix}\text{(iso) } C_3H_7 \\ \text{(iso) } C_3H_7\end{matrix}\!>N-CH_2-\underset{\displaystyle Br}{C}=CH \;+\; 2\,NaNH_2 \longrightarrow$$

$$\begin{matrix}\text{(iso) } C_3H_7 \\ \text{(iso) } C_3H_7\end{matrix}\!>N-CH_2-C\equiv C-Na \;+\; NaBr \;+\; 2\,NH_3$$

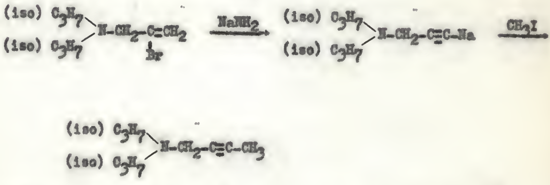
Seventy grams (3.04 moles) of metallic sodium were converted into sodium amide in liquid ammonia, and the resulting sodium amide was reacted for a period of nine hours in liquid ammonia with 290 g. (1.32 moles) of 1-diisopropylamino-2-bromopropene-2. The isolation of the product was carried out in the manner previously described.

Fractionation yielded 149 g. of 1-diisopropylamino-propyne-2, boiling from 152.5-153° (corr.). This yield corresponded to 81.5% of the theoretical amount, based upon the 1-diisopropylamino-2-bromopropene-2 used.

The following physical constants and analytical data were determined for this compound:

B.p.	152.5-153° (corr.)
n_D^{25}	1.4385
D_4^{25}	0.8017
Mr_D	Theoretical, 45.70; found, 45.64
N, %	Theoretical, 10.06; found, 10.19

Synthesis of 1-Diisopropylamino-butyne-2



$$\begin{matrix}(iso)\ C_3H_7 \\ (iso)\ C_3H_7\end{matrix}\!>N-CH_2-\underset{Br}{C}=CH_2 \xrightarrow{NaNH_2} \begin{matrix}(iso)\ C_3H_7 \\ (iso)\ C_3H_7\end{matrix}\!>N-CH_2-C\equiv C-Na \xrightarrow{CH_3I}$$

$$\begin{matrix}(iso)\ C_3H_7 \\ (iso)\ C_3H_7\end{matrix}\!>N-CH_2-C\equiv C-CH_3$$

Fifty-three grams (2.3 moles) of metallic sodium were converted into sodium amide in liquid ammonia, and the resulting sodium amide was reacted for nine hours in liquid ammonia with 220 g. (1 mole) of 1-diisopropylamino-2-bromopropene-2. One hundred and eighty-five grams (1.3 moles) of methyl iodide were then added into the flask, and stirring was continued for a period of five hours after completion of the addition. The isolation of the product was carried out as previously described.

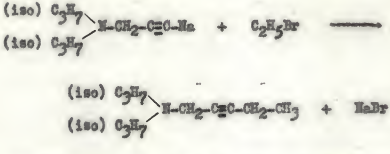
Fractionation yielded 54 g. of 1-diisopropylamino-propyne-2 (39% yield from starting product) and 65 g. of 1-diisopropylamino-butyne-2, boiling from 64-65° (corr.)/10 mm. This yield corresponded to 43% of the theoretical amount, based upon the 1-diisopropylamino-2-bromopropene-2 used.

The following physical constants and analytical data were determined for this compound:

B.p.	64-65° (corr.)/10 mm.
n_D^{25}	1.4482
D_4^{25}	0.8209
Mr_D	Theoretical, 50.32; found, 49.97
N, %	Theoretical, 9.14; found, 9.03

It may be seen from the result of the fractionation that the introduction of the triple bond proceeded in 82% yield but that the coupling of methyl iodide should have been allowed more time, since it proceeded only in 43% yield.

Synthesis of 1-Diisopropylamino-pentyne-2



$$\begin{matrix}(\text{iso})\ C_3H_7 \\ (\text{iso})\ C_3H_7\end{matrix}\!\!>N-CH_2-C\equiv C-Na \quad + \quad C_2H_5Br \longrightarrow$$

$$\begin{matrix}(\text{iso})\ C_3H_7 \\ (\text{iso})\ C_3H_7\end{matrix}\!\!>N-CH_2-C\equiv C-CH_2-CH_3 \quad + \quad NaBr$$

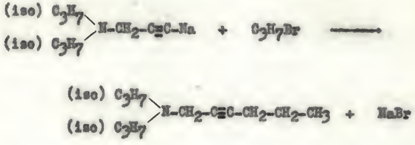
Fourteen grams (0.61 mole) of metallic sodium were converted into sodium amide in liquid ammonia, and the resulting sodium amide was reacted for one hour in liquid ammonia with 80 g. (0.575 mole) of 1-diisopropylamine-propyne-2. Sixty-six and one-half grams (0.61 mole) of ethyl bromide were then added into the flask and stirring was continued for a period of twelve hours after the completion of the addition. The isolation of the product was carried out as previously described.

Fractionation yielded 65 g. of 1-diisopropylamino-pentyne-2, boiling from 75.5-76° (corr.)/10 mm. This yield corresponded to 68% of the theoretical amount, based upon the 1-diisopropylamino-propyne-2 used.

The following physical constants and analytical data were determined for this compound:

B.p.	75.5-76° (corr.)/10 mm.
n_D^{25}	1.4470
D_4^{25}	0.8146
Mr_D	Theoretical, 54.94; found, 54.94
N,%	Theoretical, 8.37; found, 8.38

Synthesis of 1-Diisopropylamino-hexyne-2



$$\left.\begin{matrix}(\text{iso})\ C_3H_7\\(\text{iso})\ C_3H_7\end{matrix}\right\rangle N-CH_2-C\equiv C-Na \quad + \quad C_3H_7Br \longrightarrow$$

$$\left.\begin{matrix}(\text{iso})\ C_3H_7\\(\text{iso})\ C_3H_7\end{matrix}\right\rangle N-CH_2-C\equiv C-CH_2-CH_2-CH_3 \quad + \quad NaBr$$

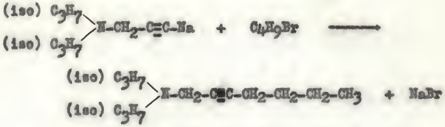
Fourteen grams (0.61 mole) of metallic sodium were converted into sodium amide in liquid ammonia, and the resulting sodium amide was reacted for one hour in liquid ammonia with 80 g. (0.575 mole) of 1-diisopropylamino-propyne-2. Seventy-five grams (0.61 mole) of n-propyl bromide were then added into the flask, and stirring was continued for a period of twelve hours after the completion of the addition. The isolation of the product was carried out in the manner previously described.

Fractionation yielded 64.5 g. of 1-diisopropylamino-hexyne-2, boiling from 89-90° (corr.)/10 mm. This yield corresponded to 62% of the theoretical amount, based upon the 1-diisopropylamino-propyne-2 used.

The following physical constants and analytical data were determined for this compound:

B.p.	89-90° (corr.)/10 mm.
n_D^{25}	1.4490
D_4^{25}	0.8182
Mr_D	Theoretical, 59.55; found, 59.44
N, %	Theoretical, 7.73; found, 7.75

Synthesis of 1-Diisopropylamino-heptyne-2



$$\begin{matrix}\text{(iso) } C_3H_7\\ \text{(iso) } C_3H_7\end{matrix}\!\!>\!N-CH_2-C\equiv C-Na \quad + \quad C_4H_9Br \quad \longrightarrow$$

$$\begin{matrix}\text{(iso) } C_3H_7\\ \text{(iso) } C_3H_7\end{matrix}\!\!>\!N-CH_2-C\equiv C-CH_2-CH_2-CH_2-CH_3 \quad + \quad NaBr$$

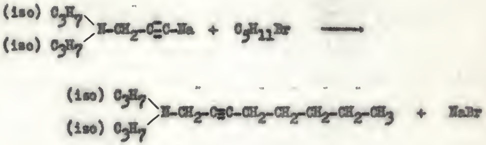
Sixteen and six-tenths grams (0.72 mole) of metallic sodium were converted into sodium amide in liquid ammonia, and the resulting sodium amide was reacted for one hour in liquid ammonia with 97.5 g. (0.7 mole) of 1-diisopropylamino-propyne-2. Ninety-eight and one-half grams (0.72 mole) of n-butyl bromide were then added into the flask, and stirring was continued for a period of twelve hours after the completion of the addition. The isolation of the product was carried out as previously described.

Fractionation yielded 85 g. of 1-diisopropylamino-heptyne-2, boiling at 103° (corr.)/10 mm. This yield corresponded to 62% of the theoretical amount, based upon the 1-diisopropylamino-propyne-2 used.

The following physical constants and analytical data were determined for this compound:

B.p.	103°(corr.)/10 mm.
n_D^{25}	1.4505
D_4^{25}	0.8200
Mr_D	Theoretical, 64.17; found, 64.09
N, %	Theoretical, 7.17; found, 7.27

Synthesis of 1-Diisopropylamino-octyne-2



$$\left.\begin{matrix}\text{(iso) } C_3H_7 \\ \text{(iso) } C_3H_7\end{matrix}\right> N-CH_2-C\equiv C-Na \; + \; C_5H_{11}Br \longrightarrow$$

$$\left.\begin{matrix}\text{(iso) } C_3H_7 \\ \text{(iso) } C_3H_7\end{matrix}\right> N-CH_2-C\equiv C-CH_2-CH_2-CH_2-CH_2-CH_3 \; + \; NaBr$$

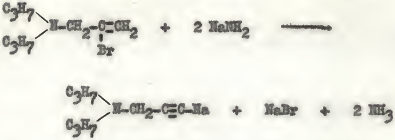
Sixteen grams (0.7 mole) of metallic sodium were converted into sodium amide in liquid ammonia, and the resulting sodium amide was reacted for one hour in liquid ammonia with 69.5 g. (0.5 mole) of 1-diisopropylamino-propyne-2. One hundred and six grams (0.7 mole) of n-amyl bromide were then added into the flask, and stirring was continued for a period of twelve hours after the completion of the addition. The isolation of the product was carried out as previously described.

Fractionation yielded 69 g. of 1-diisopropylamino-octyne-2, boiling from 115.5-116.5° (corr.)/10 mm. This yield corresponded to 66% of the theoretical amount, based upon the 1-diisopropylamino-propyne-2 used.

The following physical constants and analytical data were determined for this compound:

B.p.	115.5-116.5° (corr.)/10 mm.
n_D^{25}	1.4515
D_4^{25}	0.8203
Mr_D	Theoretical, 68.79; found, 68.79
N, %	Theoretical, 6.69; found, 6.71

Synthesis of 1-Dipropylamino-propyne-2



$$(C_3H_7)_2N-CH_2-\underset{\displaystyle Br}{C}=CH_2 + 2\ NaNH_2 \longrightarrow (C_3H_7)_2N-CH_2-C\equiv C-Na + NaBr + 2\ NH_3$$

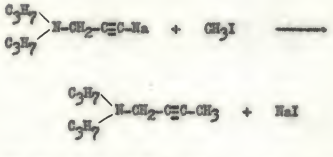
Eighty grams (3.48 moles) of metallic sodium were converted into sodium amide in liquid ammonia, and the resulting sodium amide was reacted for twelve hours in liquid ammonia with 330 g. (1.5 moles) of 1-dipropylamino-2-bromopropene-2. The isolation of the product was carried out in the manner previously described.

Fractionation yielded 169 g. of 1-dipropylamino-propyne-2, boiling from 157.5-158.5° (corr.). This yield corresponded to 81% of the theoretical amount, based upon the 1-dipropylamino-2-bromopropene-2 used.

The following physical constants and analytical data were determined for this compound:

B.p.	157.5-158.5° (corr.)
n_D^{25}	1.4325
D_4^{25}	0.7986
Mr_D	Theoretical, 45.70; found, 45.26
N, %	Theoretical, 10.06; found, 10.09

Synthesis of 1-Dipropylamino-butyne-2



$$(C_3H_7)_2N\text{-}CH_2\text{-}C{\equiv}C\text{-}Na \; + \; CH_3I \longrightarrow (C_3H_7)_2N\text{-}CH_2\text{-}C{\equiv}C\text{-}CH_3 \; + \; NaI$$

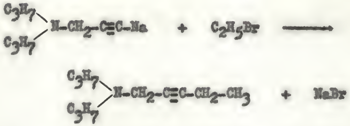
Sixteen grams (0.695 mole) of metallic sodium were converted into sodium amide in liquid ammonia, and the resulting sodium amide was reacted for one hour in liquid ammonia with 80 g. (0.575 mole) of 1-dipropylamino-propyne-2. Ninety-nine grams (0.695 mole) of methyl iodide were then added into the flask, and stirring was continued for twelve hours after the completion of the addition. The isolation of the product was carried out as previously described.

Fractionation yielded 71 g. of 1-dipropylamino-butyne-2, boiling from 70-70.5° (corr.)/10 mm. This yield corresponded to 81% of the theoretical amount, based upon the 1-dipropylamino-propyne-2 used.

The following physical constants and analytical data were determined for this compound:

B.p.	70-70.5° (corr.)/10 mm.
n_D^{25}	1.4431
D_4^{25}	0.8090
Mr_D	Theoretical, 50.32; found, 50.24
N, %	Theoretical, 9.14; found, 9.09

Synthesis of 1-Dipropylamino-pentyne-2



$$\begin{matrix} C_3H_7 \\ C_3H_7 \end{matrix}\!>\!N\text{-}CH_2\text{-}C\equiv C\text{-}Na + C_2H_5Br \longrightarrow \begin{matrix} C_3H_7 \\ C_3H_7 \end{matrix}\!>\!N\text{-}CH_2\text{-}C\equiv C\text{-}CH_2\text{-}CH_3 + NaBr$$

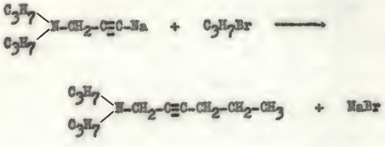
Sixteen grams (0.695 mole) of metallic sodium were converted into sodium amide in liquid ammonia, and the resulting sodium amide was reacted for one hour in liquid ammonia with 80 g. (0.575 mole) of 1-dipropylamino-propyne-2. Seventy-six grams (0.695 mole) of ethyl bromide were then added into the flask, and stirring was continued for twelve hours after the completion of the addition. The isolation of the product was carried out as previously described.

Fractionation yielded 79 g. of 1-dipropylamino-pentyne-2, boiling from 81-81.5° (corr.)/10 mm. This yield corresponded to 82.5% of the theoretical amount, based upon the 1-dipropylamino-propyne-2 used.

The following physical constants and analytical data were determined for this compound:

B.p.	81-81.5° (corr.)/10 mm.
n_D^{25}	1.4423
D_4^{25}	0.8040
Mr_D	Theoretical, 54.94; found, 55.09
N, %	Theoretical, 8.37; found, 8.42

Synthesis of 1-Dipropylamino-hexyne-2



$$\begin{matrix} C_3H_7 \\ C_3H_7 \end{matrix} \!\!>\! N-CH_2-C{\equiv}C-Na \quad + \quad C_3H_7Br \longrightarrow$$

$$\begin{matrix} C_3H_7 \\ C_3H_7 \end{matrix} \!\!>\! N-CH_2-C{\equiv}C-CH_2-CH_2-CH_3 \quad + \quad NaBr$$

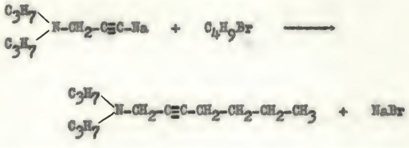
Fourteen grams (0.61 mole) of metallic sodium were converted into sodium amide in liquid ammonia, and the resulting sodium amide was reacted for one hour in liquid ammonia with 70 g. (0.503 mole) of 1-dipropylamino-propyne-2. Seventy-five grams (0.61 mole) of n-propyl bromide were then added into the flask, and stirring was continued for a period of twelve hours after the completion of the addition. The isolation of the product was carried out as described previously.

Fractionation yielded 68 g. of 1-dipropylamino-hexyne-2, boiling from 94-95° (corr.)/10 mm. This yield corresponded to 75% of the theoretical amount, based upon the 1-dipropylamino-propyne-2 used.

The following physical constants and analytical data were determined for this compound:

B.p.	94-95° (corr.)/10 mm.
n_D^{25}	1.4441
D_4^{25}	0.8066
Mr_D	Theoretical, 59.55; found, 59.73
N, %	Theoretical, 7.73; found, 7.52

Synthesis of 1-Dipropylamino-heptyne-2



$$\genfrac{}{}{0pt}{}{C_3H_7}{C_3H_7}\!>\!N-CH_2-C\equiv C-Na \;+\; C_4H_9Br \longrightarrow \genfrac{}{}{0pt}{}{C_3H_7}{C_3H_7}\!>\!N-CH_2-C\equiv C-CH_2-CH_2-CH_2-CH_3 \;+\; NaBr$$

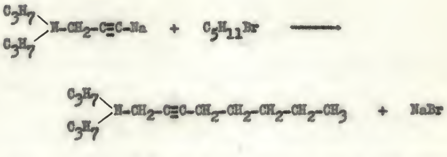
Fourteen grams (0.61 mole) of metallic sodium were converted into sodium amide in liquid ammonia, and the resulting sodium amide was reacted for one hour in liquid ammonia with 70 g. (0.503 mole) of 1-dipropylamino-propyne-2. Eighty-eight and one-half grams (0.61 mole) of n-butyl bromide were then added into the flask, and stirring was continued for a period of twelve hours after the completion of the addition. The isolation of the product was carried out as previously described.

Fractionation yielded 75 g. of 1-dipropylamino-heptyne-2, boiling from 108-109° (corr.)/10 mm. This yield corresponded to 76% of the theoretical amount, based upon the 1-dipropylamino-propyne-2 used.

The following physical constants and analytical data were determined for this compound:

B.p.	108-109° (corr.)/10 mm.
n_D^{25}	1.4459
D_4^{25}	0.8087
Mr_D	Theoretical, 64.17; found, 64.40
N, %	Theoretical, 7.17; found, 7.27

Synthesis of 1-Dipropylamino-octyne-2



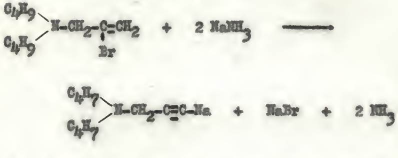
Fourteen grams (0.61 mole) of metallic sodium were converted into sodium amide in liquid ammonia, and the resulting sodium amide was reacted for one hour in liquid ammonia with 70 g. (0.503 mole) of 1-dipropylamino-propyne-2. Ninety-two grams (0.61 mole) of n-amyl bromide were then added into the flask, and stirring was continued for a period of twelve hours after completion of the addition. The isolation of the product was carried out as previously described.

Fractionation yielded 81 g. of 1-dipropylamino-octyne-2, boiling from 120.5-121.5° (corr.)/10 mm. This yield corresponded to 77% of the theoretical amount, based upon the 1-dipropylamino-propyne-2 used.

The following physical constants and analytical data were determined for this compound:

B.p.	120.5-121.5° (corr.)/10 mm.
n_D^{25}	1.4471
D_4^{25}	0.8115
Mr_D	Theoretical, 68.79; found, 68.94
N, %	Theoretical, 6.69; found, 6.94

Synthesis of 1-Dibutylamino-propyne-2



$$\begin{matrix} C_4H_9 \\ C_4H_9 \end{matrix}\Big> N\text{-}CH_2\text{-}\underset{Br}{C}{=}CH_2 \; + \; 2\ NaNH_3 \longrightarrow$$

$$\begin{matrix} C_4H_7 \\ C_4H_7 \end{matrix}\Big> N\text{-}CH_2\text{-}C{\equiv}C\text{-}Na \; + \; NaBr \; + \; 2\ NH_3$$

Eighty grams (3.48 moles) of metallic sodium were converted into sodium amide in liquid ammonia, and the resulting sodium amide was reacted for a period of twelve hours in liquid ammonia with 372 g. (1.5 moles) of 1-dibutylamino-2-bromopropene-2. The isolation of the product was carried out as described previously.

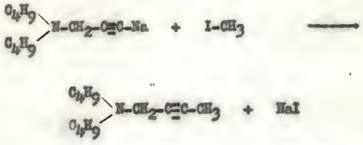
Fractionation yielded 223 g. of 1-dibutylamino-propyne-2, boiling from 77.5-78.5° (corr.)/10 mm. This yield corresponded to 89% of the theoretical amount, based upon the 1-dibutylamino-2-bromopropene-2 used.

The following physical constants and analytical data were determined for this compound:

B.p.	77.5-78.5° (corr.)/10 mm.
n_D^{25}	1.4381
D_4^{25}	0.8045
Mr_D	Theoretical, 54.93; found, 54.59
N, %	Theoretical, 8.37; found, 8.13

This compound has been previously reported in the literature,[5] but has not been prepared in this manner.

Synthesis of 1-Dibutylamino-butyne-2



$$\begin{matrix} C_4H_9 \\ C_4H_9 \end{matrix}\!>\!N-CH_2-C\equiv C-Na \;+\; I-CH_3 \longrightarrow \begin{matrix} C_4H_9 \\ C_4H_9 \end{matrix}\!>\!N-CH_2-C\equiv C-CH_3 \;+\; NaI$$

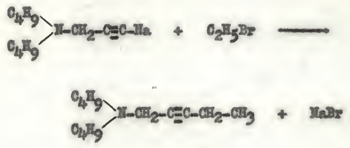
Fifteen grams (0.65 mole) of metallic sodium were converted into sodium amide in liquid ammonia, and the resulting sodium amide was reacted in liquid ammonia for one hour with 100 g. (0.60 mole) of 1-dibutylamino-propyne-2. Ninety-two and three-tenths grams (0.65 mole) of methyl iodide were then added into the flask, and stirring was continued for a period of twelve hours after the completion of the addition. The isolation of the product was carried out as previously described.

Fractionation yielded 82 g. of 1-dibutylamino-butyne-2, boiling from 97.5-97.8° (corr.)/10 mm. This yield corresponded to 75% of the theoretical amount, based upon the 1-dibutylamino-propyne-2 used.

The following physical constants and analytical data were determined for this compound:

B.p.	97.5-97.8° (corr.)/10 mm.
n_D^{25}	1.4465
D_4^{25}	0.8139
Mr_D	Theoretical, 59.55; found, 59.46
N, %	Theoretical, 7.73; found, 7.73

Synthesis of 1-Dibutylamino-pentyne-2



$$(C_4H_9)_2N-CH_2-C{\equiv}C-Na \quad + \quad C_2H_5Br \longrightarrow (C_4H_9)_2N-CH_2-C{\equiv}C-CH_2-CH_3 \quad + \quad NaBr$$

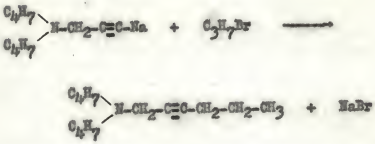
Fourteen grams (0.61 mole) of metallic sodium were converted into sodium amide in liquid ammonia, and the resulting sodium amide was reacted in liquid ammonia for one hour with 100 g. (0.60 mole) of 1-dibutylamino-propyne-2. Sixty-six and one-half grams (0.61 mole) of ethyl bromide were then added into the flask, and stirring was continued for a period of twelve hours after the completion of the addition. The isolation of the product was carried out as previously described.

Fractionation yielded 89 g. of 1-dibutylamino-pentyne-2, boiling from 107-107.2° (corr.)/10 mm. This yield corresponded to 76% of the theoretical amount, based upon the 1-dibutylamino-propyne-2 used.

The following physical constants and analytical data were determined for this compound:

B.p.	107-107.2° (corr.)/10 mm.
n_D^{25}	1.4455
D_4^{25}	0.8090
Mr_D	Theoretical, 64.17; found, 64.33
N, %	Theoretical, 7.17; found, 6.92

Synthesis of 1-Dibutylamino-hexyne-2



$$\begin{matrix}C_4H_7\diagdown\\ \quad N{-}CH_2{-}C{\equiv}C{-}Na\\ C_4H_7\diagup\end{matrix} + C_3H_7Br \longrightarrow \begin{matrix}C_4H_7\diagdown\\ \quad N{-}CH_2{-}C{\equiv}C{-}CH_2{-}CH_2{-}CH_3\\ C_4H_7\diagup\end{matrix} + NaBr$$

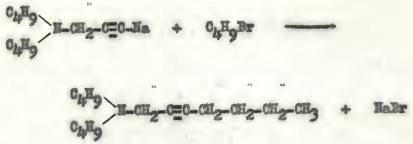
Fourteen grams (0.61 mole) of metallic sodium were converted into sodium amide in liquid ammonia, and the resulting sodium amide was reacted in liquid ammonia for one hour with 83.5 g. (0.5 mole) of 1-dibutylamino-propyne-2. Seventy-four grams (0.61 mole) of n-propyl bromide were then added into the flask, and stirring was continued for a period of twelve hours after completion of the addition. The isolation of the product was carried out as previously described.

Fractionation yielded 75 g. of 1-dibutylamino-hexyne-2, boiling from 119.5-119.8° (corr.)/10 mm. This yield corresponded to 72% of the theoretical amount, based upon the 1-dibutylamino-propyne-2 used.

The following physical constants and analytical data were determined for this compound:

B.p.	119.5-119.8° (corr.)/10 mm.
n_D^{25}	1.4472
D_4^{25}	0.8813
Mr_D	Theoretical, 68.79; found, 68.98
N, %	Theoretical, 6.69; found, 6.65

Synthesis of 1-Dibutylamino-heptyne-2



$$(C_4H_9)_2N-CH_2-C\equiv C-Na + C_4H_9Br \longrightarrow (C_4H_9)_2N-CH_2-C\equiv C-CH_2-CH_2-CH_2-CH_3 + NaBr$$

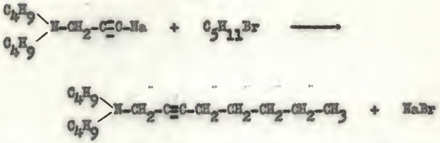
Fourteen grams (0.61 mole) of metallic sodium were converted into sodium amide in liquid ammonia, and the resulting sodium amide was reacted in liquid ammonia for one hour with 83.5 g. (0.5 mole) of 1-dibutylamino-propyne-2. Eighty-two and one-half grams of n-butyl bromide were then added into the flask, and stirring was continued for a period of twelve hours after the completion of the addition. The isolation of the product was carried out as previously described.

Fractionation yielded 84 g. of 1-dibutylamino-heptyne-2, boiling from 131.6-132.2° (corr.)/10 mm. This yield corresponded to 75.5% of the theoretical amount, based upon the 1-dibutylamino-propyne-2 used.

The following physical constants and analytical data were determined for this compound:

B.p.	131.6-132.2° (corr.)/10 mm.
n_D^{25}	1.4483
D_4^{25}	0.8127
Mr_D	Theoretical, 73.41; found, 73.63
N, %	Theoretical, 6.27; found, 6.26

Synthesis of 1-Dibutylamino-octyne-2



$$(C_4H_9)_2N\text{-}CH_2\text{-}C{\equiv}C\text{-}Na + C_5H_{11}Br \longrightarrow (C_4H_9)_2N\text{-}CH_2\text{-}C{\equiv}C\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3 + NaBr$$

Fourteen grams (0.61 mole) of metallic sodium were converted into sodium amide in liquid ammonia, and the resulting sodium amide was reacted in liquid ammonia for one hour with 83.5 g. (0.5 mole) of 1-dibutylamino-propyne-2. Ninety-two grams (0.61 mole) of n-amyl bromide were then added into the flask, and stirring was continued for a period of twelve hours after the completion of the addition. The isolation of the product was carried out as previously described.

Fractionation yielded 91 g. of 1-dibutylamino-octyne-2, boiling from 143.5-143.8° (corr.)/10 mm. This yield corresponded to 77% of the theoretical amount, based upon the 1-dibutylamino-propyne-2 used.

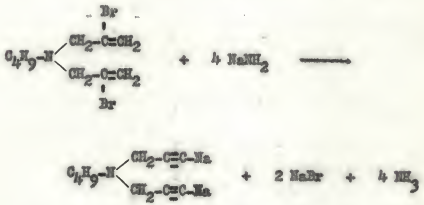
The following physical constants and analytical data were determined for this compound:

B.p.	143.5-143.8° (corr.)/10 mm.
n_D^{25}	1.4498
D_4^{25}	0.8144
Mr_D	Theoretical, 78.03; found, 78.32
N, %	Theoretical, 5.90; found, 5.84

CHAPTER V

SYNTHESIS OF TERTIARY DI - ACETYLENIC AMINES

Synthesis of N-n-Butyl-di-2-propynylamine



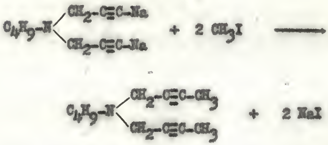
One hundred grams (4.35 moles) of metallic sodium were converted into sodium amide in liquid ammonia, and the resulting sodium amide was reacted in liquid ammonia with 406 g. (1.3 moles) of N,N-bis-(2-bromo-2-propenyl)-n-butylamine for a period of twelve hours. The isolation of the product was carried out as usual.

Fractionation yielded 148 g. of N-n-butyl-di-2-propynylamine, boiling from 73-74° (corr.)/10 mm. This yield corresponded to 76.5% of the theoretical amount, based upon the N,N-bis-(2-bromo-2-propenyl)-n-butylamine used.

The following physical constants and analytical data were determined for this compound:

B. p.	73-74° (corr.)/10 mm.
n_D^{25}	1.4567
D_4^{25}	0.8512
Mr_D	Theoretical, 48.31; found, 47.71
N, %	Theoretical, 9.39; found, 9.36

Synthesis of N-n-Butyl-di-2-butynylamine



$$C_4H_9-N\left\langle\begin{matrix}CH_2-C\equiv C-Na\\ CH_2-C\equiv C-Na\end{matrix}\right. + 2\ CH_3I \longrightarrow$$

$$C_4H_9-N\left\langle\begin{matrix}CH_2-C\equiv C-CH_3\\ CH_2-C\equiv C-CH_3\end{matrix}\right. + 2\ NaI$$

Fifty and one-half grams (2.2 moles) of metallic sodium were converted into sodium amide in liquid ammonia, and the resulting sodium amide was reacted for one hour in liquid ammonia with 125 g. (0.84 mole) of N-n-butyl-di-2-propynylamine. Three hundred and ten grams (2.2 moles) of methyl iodide were then added into the flask, and stirring was continued for a period of eight hours after completion of the addition. The isolation of the product was carried out as previously described.

Fractionation yielded 107 g. of N-n-butyl-di-2-butynylamine, boiling from 114.5-115.5° (corr.)/10 mm. This yield corresponded to 72% of the theoretical amount, based upon the N-n-butyl-di-2-propynylamine used.

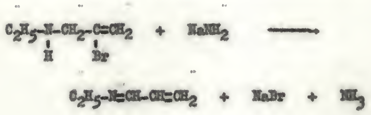
The following physical constants and analytical data were determined for this compound:

B.p.	114.5-115.5° (corr.)/10 mm.
n_D^{25}	1.4778
D_4^{25}	0.8616
Mr_D	Theoretical, 57.56; found, 58.20
N, %	Theoretical, 7.90; found, 7.80

CHAPTER VI

SYNTHESIS OF N-SUBSTITUTED 2-PROPENYLIDENIMINES

Synthesis of N-2-Propenylidene-ethylamine



$$C_2H_5\text{-}\underset{H}{\underset{|}{N}}\text{-}CH_2\text{-}\underset{Br}{\underset{|}{C}}{=}CH_2 + NaNH_2 \longrightarrow C_2H_5\text{-}N{=}CH\text{-}CH{=}CH_2 + NaBr + NH_3$$

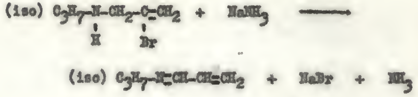
Sixty-four grams (2.78 moles) of metallic sodium were converted into sodium amide in liquid ammonia, and the resulting sodium amide was reacted for ten hours in liquid ammonia with 350 g. (2.14 moles) of 1-ethylamino-2-bromopropene-2. The isolation of the product was carried out as previously described.

Fractionation yielded 97 g. of N-2-propenylidene-ethylamine, boiling from 77.2-77.5° (corr.). This yield corresponded to 55% of the theoretical amount, based upon the 1-ethylamino-2-bromopropene-2 used.

The following physical constants and analytical data were determined for this compound:

B.p.	77.2-77.5° (corr.)
n_D^{25}	1.4284
D_4^{25}	0.7795
Mr_D	Theoretical, 27.50; found, 27.46
N, %	Theoretical, 16.85; found, 16.76

Synthesis of N-2-Propenylidene-isopropylamine



$$\text{(iso) } C_3H_7\text{-}\underset{\displaystyle H}{\underset{|}{N}}\text{-}CH_2\text{-}\underset{\displaystyle Br}{\underset{|}{C}}{=}CH_2 + NaNH_3 \longrightarrow$$

$$\text{(iso) } C_3H_7\text{-}N{=}CH\text{-}CH{=}CH_2 + NaBr + NH_3$$

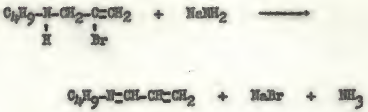
Forty-three grams (1.87 moles) of metallic sodium were converted into sodium amide in liquid ammonia, and the resulting sodium amide was reacted for ten hours in liquid ammonia with 256 g. (1.44 moles) of 1-isopropylamino-2-bromopropene-2. The isolation of the product was carried out as usual.

Fractionation yielded 80 g. of N-2-propenylidene-isopropylamine, boiling from 93-94° (corr.). This yield corresponded to 57% of the theoretical amount, based upon the 1-isopropylamino-2-bromopropene-2 used.

The following physical constants and analytical data were determined for this compound:

B.p.	93-94° (corr.)
n_D^{25}	1.4269
D_4^{25}	0.7759
Mr_D	Theoretical, 32.12; found, 32.14
N, %	Theoretical, 14.42; found, 14.44

Synthesis of N-2-Propenylidene-n-butylamine



$$C_4H_9\text{-}\underset{H}{N}\text{-}CH_2\text{-}\underset{Br}{C}{=}CH_2 + NaNH_2 \longrightarrow$$

$$C_4H_9\text{-}N{=}CH\text{-}CH{=}CH_2 + NaBr + NH_3$$

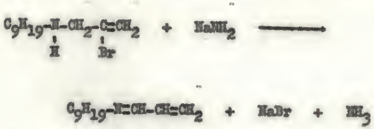
Forty-three and seven-tenths grams (1.9 moles) of metallic sodium were converted into sodium amide in liquid ammonia, and the resulting sodium amide was reacted for twelve hours in liquid ammonia with 320 g. (1.667 moles) of 1-n-butylamino-2-bromopropene-2. The isolation of the product was carried out as previously described.

Fraction yielded 142 g. of N-2-propenylidene-n-butylamine, boiling from 129.5-130.5° (corr.). This yield corresponded to 77% of the theoretical amount, based upon the 1-n-butylamino-2-bromopropene-2 used.

The following physical constants and analytical data were determined for this compound:

B.p.	129.5-130.5° (corr.)
n_D^{25}	1.4375
D_4^{25}	0.7941
Mr_D	Theoretical, 36.73; found, 36.72
N, %	Theoretical, 12.60; found, 12.58

Synthesis of N-2-Propenylidene-nonylamine



$$C_9H_{19}-\underset{H}{N}-CH_2-\underset{Br}{C}=CH_2 \quad + \quad NaNH_2 \longrightarrow$$

$$C_9H_{19}-N=CH-CH=CH_2 \quad + \quad NaBr \quad + \quad NH_3$$

Twenty-six and one-half grams (1.15 moles) of metallic sodium were converted into sodium amide in liquid ammonia, and the resulting sodium amide was reacted for twelve hours in liquid ammonia with 167 g. (0.64 mole) of 1-nonylamino-2-bromopropene-2. The isolation of the product was carried out as previously described.

Fractionation yielded 84 g. of N-2-propenylidene-nonylamine, boiling from 86.5-87.5° (corr.)/10 mm. This yield corresponded to 72% of the theoretical amount, based upon the 1-nonylamino-2-bromopropene-2 used.

The following physical constants and analytical data were determined for this compound:

B.p.	86.5-87.5° (corr.)/10 mm.
n_D^{25}	1.4489
D_4^{25}	0.8113
Mr_D	Theoretical, 59.93; found, 59.93
N, %	Theoretical, 7.73; found, 7.83

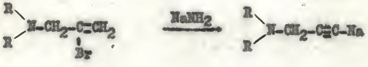
CHAPTER VII

THEORETICAL ASPECTS OF THE DEHYDROHALOGENATION OF HALO-ALKENYLAMINES WITH SODIUM AMIDE IN LIQUID AMMONIA

A. Summary of the Various Types of Dehydrohalogenation Reactions Described in this Dissertation, with Establishment of Structure of Resulting Compounds

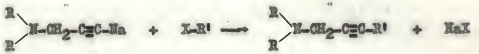
Before any mechanisms may be proposed for these dehydrohalogenation reactions, it is necessary to present a summary of the three types of dehydrohalogenations carried out and the results obtained, together with the evidence supporting these results.

The first reactions carried out were the dehydrohalogenations of tertiary halo-alkenylamines containing two similar alkyl groups and the 2-bromo-2-propenyl radical on the nitrogen atom. These compounds, on dehydrohalogenation, yielded tertiary, acetylenic amines, as illustrated in equation (1):



$$R_2N\text{-}CH_2\text{-}C(Br){=}CH_2 \xrightarrow{NaNH_2} R_2N\text{-}CH_2\text{-}C{\equiv}C\text{-}Na \qquad (1)$$

The sodium acetylides formed were readily decomposed to the free amine by water. The reactions were clear-cut, and it is unnecessary to present proof of structure of the resulting compounds, since similar reactions are well-known in the hydrocarbon series and since various alkyl halides have been coupled to the sodium acetylides of these compounds to yield the expected product, in accordance with equation (2):

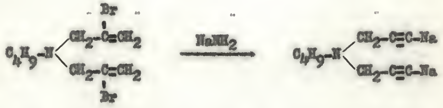


$$\left.\begin{matrix}R\\ R\end{matrix}\right>N\text{-}CH_2\text{-}C{\equiv}C\text{-}Na \;+\; X\text{-}R' \longrightarrow \left.\begin{matrix}R\\ R\end{matrix}\right>N\text{-}CH_2\text{-}C{\equiv}C\text{-}R' \;+\; NaX$$

(2)

The fact that the reaction represented by equation (2) proceeds is sufficient proof of the existence of a terminal triple bond. Furthermore, 1-diethylamino-propyne-2 has been synthesized in the manner shown by equation (1), and its boiling point coincides with that reported in the literature.^{6} The physical constants of 1-diethylamino-heptyne-2, prepared in accordance with equation (2), agree with those previously reported.^{2}

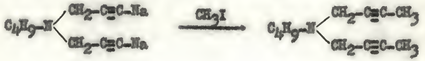
The second type of dehydrohalogenation which was carried out was that of N,N-bis-(2-bromo-2-propenyl)-n-butylamine, as shown in equation (3):



$$C_4H_9\text{-}N\left<\begin{matrix}CH_2\text{-}\overset{Br}{C}{=}CH_2\\ CH_2\text{-}\underset{Br}{C}{=}CH_2\end{matrix}\right. \xrightarrow{NaNH_2} C_4H_9\text{-}N\left<\begin{matrix}CH_2\text{-}C{\equiv}C\text{-}Na\\ CH_2\text{-}C{\equiv}C\text{-}Na\end{matrix}\right.$$

(3)

There can be little doubt that the resulting compound is actually N-n-butyl-di-2-propynylamine, since the diacetylide of this compound was coupled with methyl iodide to yield N-n-butyl-di-2-butynylamine:

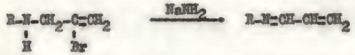


$$C_4H_9\text{-}N\left<\begin{matrix}CH_2\text{-}C{\equiv}C\text{-}Na\\ CH_2\text{-}C{\equiv}C\text{-}Na\end{matrix}\right. \xrightarrow{CH_3I} C_4H_9\text{-}N\left<\begin{matrix}CH_2\text{-}C{\equiv}C\text{-}CH_3\\ CH_2\text{-}C{\equiv}C\text{-}CH_3\end{matrix}\right.$$

(4)

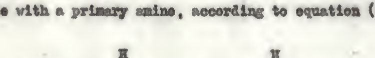
The Kjeldahl analyses of both of these compounds gave satisfactory results, and the coupling of two methyl groups, as shown in equation (4), itself clearly indicated by analysis, proves the existence of two terminal triple bonds in the original compound, N-n-butyl-di-2-propynylamine. The molar refraction calculated from the physical constants of N-n-butyl-di-2-propynylamine differed from the theoretical value by 0.60, a significant quantity. This difference will be discussed at a later point in the chapter, and an explanation will be proposed.

In an effort to prepare the corresponding secondary, acetylenic amine, a third type of dehydrohalogenation was carried out: that of a secondary halo-alkenylamine. Instead of producing the expected product, however, the reaction proceeded as shown in equation (5):



$$R-\underset{H}{N}-CH_2-\underset{Br}{C}=CH_2 \xrightarrow{NaNH_2} R-N=CH-CH=CH_2 \qquad (5)$$

It becomes necessary at this point to establish the fact that the resulting compound is that which is shown in this equation, an N-substituted 2-propenylidenimine. Compounds of this general type are also known as aldimines, or Schiff bases, and normally result from the reaction of an aldehyde with a primary amine, according to equation (6):



$$R-NH_2 + O=\overset{H}{C}-R' \longrightarrow R-N=\overset{H}{C}-R' + H_2O \qquad (6)$$

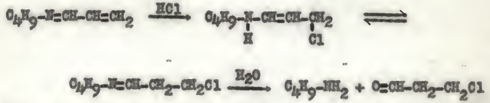
The N-substituted 2-propenylidenimines which have been prepared are those which would result from the reaction of acrolein with primary amines, if acrolein underwent the reaction shown in equation (6). It does not do so, however; its reaction with primary amines usually leads to unidentifiable resins.[40,42] Although some instances have been reported in which definite products were obtained,[41,43] these products were not the simple N-substituted 2-propenylidenimines.

After the dehydrohalogenation of the secondary halo-alkenylamine had been carried out, the resulting compound necessarily contained either a triple bond in the terminal position or two double bonds. The nonexistence of a triple bond in the terminal position was clearly indicated by failure of the compound to couple with alkyl halides after treatment with sodium amide in liquid ammonia. Two attempts were made to carry out this reaction, using different alkyl halides, but the only product obtained was the unchanged starting material. It may be safely assumed, therefore, that the compound contained two double bonds. It may also be assumed that one of these double bonds was in the terminal position, since no conditions were imposed at any time which could conceivably have shifted the original double bond of the 2-bromo-2-propenyl radical from its terminal position.

Aldimines are known to hydrolyze readily in acid solution, thus reversing equation (6), to yield the aldehyde and the amine. Treatment of one of these compounds, N-2-propenylidene-n-butylamine, with dilute hydrochloric acid decomposed the compound to yield n-butylamine and an aldehyde, thus establishing the original compound as an aldimine and locating the second double bond between the nitrogen atom and the adjacent carbon. The n-butylamine obtained was identified by boiling point and refractive index. The other hydrolysis product was identified as an aldehyde by: formation of a 2,4-dinitrophenylhydrazone, reduction of permanganate, formation of a silver mirror with Tollen's reagent, and reduction of Fehling's solution in the cold. All efforts to isolate the aldehyde formed have failed, resulting only in extensive decomposition.

The hydrolysis of N-2-propenylidene-n-butylamine in acid solution might be expected to yield n-butylamine and acrolein, but it has been established that this is not the case. The amine formed was butylamine, as previously stated, but the aldehyde did not decolorize bromine water readily, thereby eliminating acrolein as a possibility. Furthermore, it has been found that the melting point of the 2,4-dinitrophenylhydrazone derivative of this aldehyde varied with the acid used to catalyze the hydrolysis. When hydrochloric acid was used, the 2,4-dinitrophenylhydrazone derivative of the aldehyde melted from 124-125° and was found to contain chlorine. This derivative in aqueous solution gave no precipitate with aqueous silver nitrate; therefore, the chlorine was not of ionic character. When sulfuric acid was used to catalyze the hydrolysis, the 2,4-dinitrophenylhydrazone of the resulting aldehyde melted above 200° and was found to contain sulfur.

From the above information, it might seem probable that the hydrolysis of these compounds in acid solution would proceed in the following manner:



$$C_4H_9\text{-}N{=}CH\text{-}CH{=}CH_2 \xrightarrow{HCl} C_4H_9\text{-}\underset{\displaystyle H}{\underset{|}{N}}\text{-}CH{=}CH\text{-}\underset{\displaystyle Cl}{\underset{|}{CH_2}} \rightleftharpoons$$

$$C_4H_9\text{-}N{=}CH\text{-}CH_2\text{-}CH_2Cl \xrightarrow{H_2O} C_4H_9\text{-}NH_2 + O{=}CH\text{-}CH_2\text{-}CH_2Cl \qquad (7)$$

The first step in the hydrolysis shown would be the 1,4-addition of hydrogen chloride. This is logical, realizing the ease with which

1,4-additions to conjugated double bonds occur. The second step would be the rearrangement of an alpha-beta-unsaturated amine to the corresponding imine, also a well-known reaction.[44,45,46] The final step would be hydrolysis of the imine to yield an amine and 3-chloro-propionaldehyde. It has been established that this probably does not occur, however. A 2,4-dinitrophenylhydrazone prepared from a known sample of the diethyl acetal of 3-chloro-propionaldehyde melted from 121-122°; the 2,4-dinitrophenylhydrazone prepared from N-2-propenylidene-ethylamine melted from 123-124°. The mixed melting point of the two derivatives was 101-104°, indicating that the hydrolysis product probably was not 3-chloro-propionaldehyde. The mechanism of this hydrolysis and the resulting product are unknown.

An attempt to reduce N-2-propenylidene-n-butylamine with lithium aluminum hydride resulted only in the formation of a considerable quantity of material boiling above 250°, probably a polymer, and in recovery of some unchanged material.

Kjeldahl analyses of these compounds gave satisfactory results, and the molar refractions calculated from their physical constants are in almost exact agreement with the theoretical values.

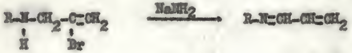
N-2-Propenylidene-n-butylamine gave several reactions which are characteristic of acrolein: a good iodoform test; evolution of excessive heat when treated with saturated sodium bisulfite solution, with no precipitate forming immediately; and rapid decolorization of a solution of bromine in carbon tetrachloride.

The 2,4-dinitrophenylhydrazones prepared from N-2-propenylidene-n-butylamine and from N-2-propenylidene-ethylamine were established as identical by melting points and mixed melting point, eliminating any possibility that the 2,4-dinitrophenylhydrazine forms a derivative with the entire imine molecule, rather than with only the aldehyde portion.

Although no single item of experimental data can be offered as conclusive proof of the structure of these compounds, their structure is sufficiently proven by the experimental evidence given on the preceeding pages.

B. Proposed Mechanism for the Dehydrohalogenation Reactions Described in this Dissertation

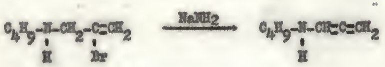
The first insight into the mechanism of these reactions is given by the unique synthesis of N-substituted 2-propenylidenimines which has been discussed. The equation for this reaction was given as equation (5) of this chapter, and is repeated here for convenience of discussion:



$$\underset{\textstyle H}{R-\overset{}{N}}-CH_2-\underset{\textstyle Br}{C}=CH_2 \xrightarrow{NaNH_2} R-N=CH-CH=CH_2 \qquad (5)$$

It is highly improbable that a hydrogen atom from the terminal carbon atom was removed with the bromine atom in the dehydrohalogenation, with subsequent rearrangement of the acetylenic linkage thus obtained to the conjugated system which actually resulted from the reaction. The acetylenic linkage would have been stabilized, if present, by the formation of the sodium acetylide under the influence of an excess of sodium amide. Furthermore, N-isobutyl-propynylamine has been reported in the literature as a stable compound, b.p. 134-136°;[6] if N-butyl-propynylamine had been formed in this reaction, it should have been isolated as such.

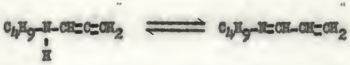
It therefore becomes evident that the hydrogen atom which was removed with the bromine atom came from the carbon atom adjacent to the nitrogen, in accordance with the following reaction:



$$C_4H_9-\underset{H}{N}-CH_2-\underset{Br}{C}=CH_2 \xrightarrow{NaNH_2} C_4H_9-\underset{H}{N}-CH=C=CH_2$$

(8)

The compound which results from this reaction is an alpha, beta-unsaturated amine, and is therefore in equilibrium with the corresponding imine:[44,45,46]



$$\underset{(I)}{C_4H_9-\underset{H}{N}-CH=C=CH_2} \rightleftharpoons \underset{(II)}{C_4H_9-N=CH-CH=CH_2}$$

(9)

(I) (II)

It would be expected that this equilibrium would be shifted far to the right because of the enhanced stability of the conjugated system and the extreme instability of the allenes. This expectation is strongly supported by molar refraction data, as presented below:

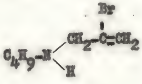
Theoretical molar refraction of Structure I..... 37.19

Theoretical molar refraction of Structure II.... 36.73

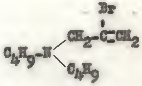
Value determined from physical constants........ 36.72

There is almost exact agreement between the theoretical and found values of molar refraction of all members of this series which have been prepared, when the theoretical values were based upon the N-substituted 2-propenylidenimine structure.

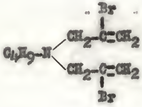
This mechanism offers a very logical explanation for the unusual products obtained in these reactions, but it makes necessary a closer examination of the mechanisms of the other dehydrohalogenations which have been carried out. The three types of halo-alkenylamines which have been dehydrohalogenated in this research are presented below:



(A)



(B)



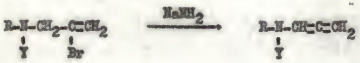
(C)

It is seen that the only difference in these compounds lies in one of the groups attached to the nitrogen in each case. In (A), above, this group is a hydrogen atom; in (B) it is an alkyl group and is more electropositive than hydrogen; in (C) it is the 2-bromo-2-propenyl radical, probably more electronegative than hydrogen, although the author of this dissertation is not equipped to make a positive assertion regarding its relative electronegativity.

It seems highly improbable that hydrogen halide would be split out in such a direction as to form the terminal triple bond in case (B), above; that it would be split out in the opposite direction to form the substituted allene in case (A), when the alkyl group has been replaced by a more electronegative group, the hydrogen atom; and that it would be again split out to form the triple bond when the alkyl group is replaced by a still more electronegative group, the 2-bromo-2-propenyl radical. The final product of dehydrohalogenation, however, is the N-substituted 2-propenylidenimine in case (A), and is the acetylenic amine in cases (B) and (C).

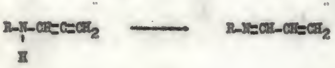
With this reasoning in mind, a mechanism for these dehydrohalogenation reactions has been conceived which fits all the known facts and probabilities. The proposed mechanism is as follows:

Treatment of N-substituted 2-bromo-2-propenylamines with sodium amide in liquid ammonia results in removal of hydrogen halide in such a direction that an allene is formed in accordance with the following equation:



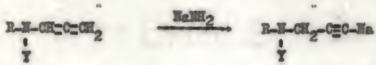
$$\underset{Y}{\underset{|}{\ddot{R-N}}}-CH_2-\underset{Br}{\underset{|}{C}}=CH_2 \xrightarrow{NaNH_2} \underset{Y}{\underset{|}{\ddot{R-N}}}-CH=C=CH_2$$

If Y represents a hydrogen atom, its mobility is such that rearrangement to the imine can occur, with the subsequent stabilization of the resulting compound by conjugation of the double bonds:



$$\underset{H}{\underset{|}{\ddot{R-N}}}-CH=C=CH_2 \longrightarrow R-\ddot{N}=CH-CH=CH_2$$

If Y, on the other hand, represents some group other than a hydrogen atom, regardless of its relative electronegativity, its lesser mobility makes this rearrangement to the imine impossible. Instead, the allene is rearranged to the acetylenic linkage under the influence of excess sodium amide and with the formation of the sodium acetylide:



$$\underset{Y}{R-\ddot{N}}-CH=C=CH_2 \xrightarrow{NaNH_2} \underset{Y}{R-\ddot{N}}-CH_2-C\equiv C-Na$$

To state this proposed theory more briefly, dehydrohalogenation of these halo-alkenylamines produces in every case an allene which rearranges. When rearrangement to the imine, with conjugation of the double bonds, is possible, this reaction takes precedence. When rearrangement to the imine is impossible, due to the absence of a hydrogen atom on the nitrogen, the rearrangement is to the acetylenic linkage. This rearrangement of allenes to triple bonds under the influence of alkali has long been known to occur. Favorsky reported the use of metallic sodium for this reaction,[47] and the use of sodium amide has also been reported.[48]

C. Discussion of Deviations in Molar Refractions

Several cases have been observed among the compounds described in this dissertation in which considerable difference existed between the observed and calculated values of molar refractions. In connection with this, it is of interest to observe the data presented in Table II.

Several interesting conclusions may be drawn from this table. It is at once seen that a definite pattern exists in these differences between observed and calculated values. Without exception, the difference is greatest in the case of the derivative of propyne-2, decreases to a minimum in the derivatives of butyne-2 or pentyne-2, and then increases again as the chain lengthens.

TABLE II

DIFFERENCES BETWEEN OBSERVED AND CALCULATED VALUES OF MOLAR REFRACTIONS OF EIGHTEEN 1-DI-n-ALKYLAMINO-2-ALKYNES[a]

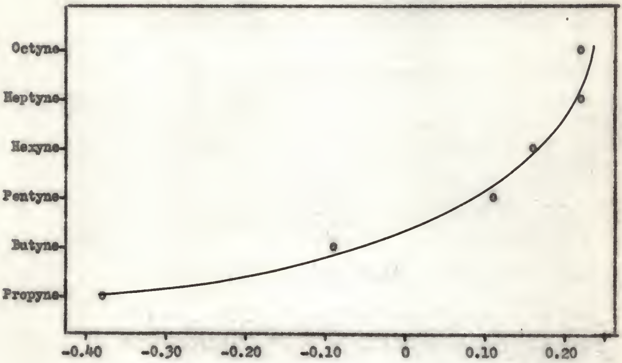
Alkyne Group	1-Di-n-alkylamino group			Average differences between observed and calculated values	Mean deviation of individual difference from average
	1-Diethyl-amino	1-Dipropyl-amino	1-Dibutyl-amino		
Propyne-2	-0.36	-0.44	-0.34	-0.38	0.04
Butyne-2	-0.11	-0.08	-0.09	-0.09	0.01
Pentyne-2	0.02	0.15	0.16	0.11	0.06
Hexyne-2	0.11	0.18	0.19	0.16	0.03
Heptyne-2	0.22	0.23	0.22	0.22	0.003
Octyne-2	0.23	0.15	0.29	0.22	0.05

[a] A minus sign indicates that the observed value was lower than the theoretical.

Another interesting fact to be noted is that the observed values of molar refraction of the propyne-2 and butyne-2 derivatives were invariably lower than the calculated values, whereas the observed values of the other derivatives were invariably higher than calculated. When the average difference between the observed and calculated values are plotted against increasing length of the alkyne chain, a relatively smooth curve is obtained. This is shown in Figure I.

FIGURE I

A GRAPHICAL PRESENTATION OF THE RELATIONSHIP BETWEEN THE DIFFERENCES IN OBSERVED AND CALCULATED MOLAR REFRACTIONS AND INCREASING LENGTH OF ALKYNE CHAIN



It is also interesting to note that the average difference between observed and calculated values in the derivatives of propyne-2 is -0.38, and to remember that the difference between observed and calculated values for the molar refraction of N-n-butyl-di-2-propynylamine was -0.60, roughly twice that which occurs in compounds containing only a single 2-propynyl radical. This evidence might offer a very possible and logical explanation of the large difference between the observed and calculated values of the molar refraction of N-n-butyl-di-2-propynylamine.

Although it is realized that there is insufficient evidence here to make a definite statement possible and that the significance of this material regarding atomic and molar refractions is open to question, the evidence does seem to indicate a well-defined pattern of influence shown by the location of the triple bond in the alkyne radical. This influence must be due to the location of the triple bond, since merely increasing the length of the chain apparently does not cause appreciable differences between observed and calculated values of molar refractions. The observed molar refraction of all the N-substituted 2-propenylidenimines prepared, with chain lengths from 2 to 9 carbon atoms in the alkyl radical, are in almost exact agreement with the theoretical values.

SUMMARY

A method has been devised for the synthesis of tertiary, acetylenic amines by the dehydrohalogenation of tertiary halo-alkenylamines with sodium amide, using liquid ammonia as a solvent. This method permits the synthesis of these compounds in good yield using only equipment normally found in an organic laboratory, whereas previous methods for their synthesis were more limited in application and often required the use of high-pressure equipment.

The sodium acetylides of the acetylenic amines prepared have been coupled with various n-alkyl halides to prepare the higher members of the series. Four series of compounds, each series containing six members, have been prepared by these methods.

The process has been extended to the synthesis of tertiary, di-acetylenic amines by preparation of two of these compounds.

A unique synthesis of N-substituted 2-propenylidenimines has been discovered. Four compounds of this type have been prepared by dehydrohalogenation of a secondary halo-alkenylamine with sodium amide in liquid ammonia.

A mechanism has been proposed which accounts for the various products obtained in the dehydrohalogenation of halo-alkenylamines with sodium amide in liquid ammonia.

The physical constants and analytical data for the acetylenic amines and the N-substituted 2-propenylidenimines which have been prepared are summarized in Table III.

TABLE III

SUMMARY OF PHYSICAL CONSTANTS AND ANALYTICAL DATA FOR SOME TERTIARY ACETYLENIC AMINES
AND SOME N-SUBSTITUTED 2-PROPENYLIDENIMINES

Compound	B.p., °C.(Corr.)	n_D^{25}	D_4^{25}	Mr_D		N, %	
				Theor.	Found	Theor.	Found
TERTIARY MONO-ACETYLENIC AMINES:							
1-Diethylamino-propyne-2	120 -121	1.4296	0.8042	36.46	36.10	12.60	12.29
1-Diethylamino-butyne-2	152.5-153	1.4413	0.8075	41.08	40.97	11.19	11.19
1-Diethylamino-pentyne-2	168.4-169.9	1.4402	0.8029	45.70	45.72	10.06	10.11
1-Diethylamino-hexyne-2	187.4-188.4	1.4431	0.8058	50.33	50.44	9.14	9.02
1-Diethylamino-hex-5-en-2-yne	52 - 53 /11 mm.	1.4452	0.8085	49.85	49.81	9.26	9.20
1-Diethylamino-heptyne-2	84 - 85 / 10 mm.	1.4450	0.8071	54.94	55.16	8.37	8.31
1-Diethylamino-octyne-2	100 / 10 mm.	1.4466	0.8097	59.55	59.78	7.73	7.69
1-Diisopropylamino-propyne-2	152.5-153	1.4385	0.8017	45.70	45.64	10.06	10.19
1-Diisopropylamino-butyne-2	64 - 65 / 10 mm.	1.4482	0.8209	50.32	49.97	9.14	9.03
1-Diisopropylamino-pentyne-2	75.5- 76 / 10 mm.	1.4470	0.8146	54.94	54.94	8.37	8.38
1-Diisopropylamino-hexyne-2	89 - 90 /10 mm.	1.4490	0.8182	59.55	59.44	7.73	7.75
1-Diisopropylamino-heptyne-2	103 /10 mm.	1.4505	0.8200	64.17	64.09	7.17	7.27
1-Diisopropylamino-octyne-2	115.5-116.5/10 mm.	1.4515	0.8203	68.79	68.79	6.69	6.71

TABLE III (Continued)

Compound	B.p., °C.(Corr.)	n_D^{25}	D_4^{25}	MR_D		N, %	
				Theor.	Found	Theor.	Found
1-Dipropylamino-propyne-2	157.5-158.5	1.4325	0.7986	45.70	45.26	10.06	10.09
1-Dipropylamino-butyne-2	70.0- 70.5/10 mm.	1.4431	0.8090	50.32	50.24	9.14	9.09
1-Dipropylamino-pentyne-2	81.0- 81.5/10 mm.	1.4423	0.8040	54.94	55.09	8.37	8.42
1-Dipropylamino-hexyne-2	94 - 95 /10 mm.	1.4441	0.8066	59.55	59.73	7.73	7.52
1-Dipropylamino-heptyne-2	108 -109 /10 mm.	1.4459	0.8087	64.17	64.40	7.17	7.27
1-Dipropylamino-octyne-2	120.5-121.5/10 mm.	1.4471	0.8115	68.79	68.94	6.69	6.94
1-Dibutylamino-propyne-2	77.5- 78.5/10 mm.	1.4381	0.8045	54.93	54.59	8.37	8.13
1-Dibutylamino-butyne-2	97.5- 97.8/10 mm.	1.4465	0.8139	59.55	59.46	7.73	7.73
1-Dibutylamino-pentyne-2	107 -107.2/10 mm.	1.4455	0.8090	64.17	64.33	7.17	6.92
1-Dibutylamino-hexyne-2	119.5-119.8/10 mm.	1.4472	0.8813	68.79	68.98	6.69	6.65
1-Dibutylamino-heptyne-2	131.6-132.2/10 mm.	1.4483	0.8127	73.41	73.63	6.27	6.26
1-Dibutylamino-octyne-2	143.5-143.8/10 mm.	1.4498	0.8144	78.03	78.32	5.90	5.84
TERTIARY DI-ACETYLENIC AMINES:							
N-n-Butyl-di-2-propynylamine	73 - 74 /10 mm.	1.4567	0.8512	48.31	47.71	9.39	9.36
N-n-Butyl-di-2-butynylamine	114.5-115.5/10 mm.	1.4778	0.8616	57.56	58.20	7.90	7.80

TABLE III (Continued)

Compound	B.p., °C. (Corr.)	n_D^{25}	D_4^{25}	MR_D		N, %	
				Theor.	Found	Theor.	Found
N-SUBSTITUTED 2-PROPENYLIDENIMINES:							
N-2-Propenylidene-ethylamine	77.2- 77.5	1.4284	0.7795	27.50	27.46	16.85	16.76
N-2-Propenylidene-isopropylamine	93 - 94	1.4269	0.7759	32.12	32.14	14.42	14.44
N-2-Propenylidene-n-butylamine	129.5-130.5	1.4375	0.7941	36.73	36.72	12.60	12.58
N-2-Propenylidene-nonylamine	86.5- 87.5/10 mm.	1.4489	0.8113	59.93	59.93	7.73	7.83

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BIOGRAPHICAL ITEMS

Mr. Robert Ford Parcell was born in Lakeland, Florida, on September 1, 1922. He attended the University of Florida from 1940 until January, 1944, at which time he received the degree of Bachelor of Science. In February, 1944, he was commissioned in the United States Naval Reserve and served until September, 1946. He then returned to the University of Florida and undertook the graduate study of organic chemistry, receiving the degree of Master of Science in February, 1948. Continuing his graduate study, he received the degree of Doctor of Philosophy in February, 1950.

He has served as an undergraduate assistant in the Department of Chemistry for one year, a graduate assistant for one and one-half years, and has held a research fellowship under the Office of Naval Research for two years. He is a member of Phi Eta Sigma, Gamma Sigma Epsilon, and Phi Kappa Phi honorary societies.

COMMITTEE REPORT

This dissertation was prepared under the direction of the Chairman of the candidate's Supervisory Committee and has been approved by all members of the committee. It was submitted to the Graduate Council and was approved as partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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